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THE SYNTHESIS, PURIFICATION, AND CERTAIN PHYSICAL CONSTANTS OF THE NORMAL HYDROCARBONS FROM PENTANE TO DODECANE, OF *n*-AMYL BROMIDE AND OF *n*-NONYL BROMIDE[1]

By B. J. Mair

ABSTRACT

The normal paraffin hydrocarbons from pentane to dodecane, *n*-amyl bromide and *n*-nonyl bromide have been synthesized and prepared in very pure condition. The boiling points, freezing points, and refractive indices (N_D^{25}) of these compounds have been measured and the values compared with those obtained by other investigators on hydrocarbons isolated from petroleum. Two crystalline modifications of *n*-nonyl bromide freezing at −29.06° and −30.71° C., respectively, were discovered.

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I. INTRODUCTION

An investigation on the electrical properties of insulating liquids in progress at this bureau necessitated the preparation of some very pure hydrocarbons. The normal paraffin hydrocarbons were selected because the resistivities of liquids in this series are among the highest known, and because an interpretation of the electrical properties of liquids in terms of molecular structure should be more readily accomplished with their simple molecules than with molecules of more complex structure. All the members of this series from pentane to dodecane were prepared. An examination of the literature when this work was begun showed that many of the physical properties of these substances were not well established. Recently, however, Shepard, Henne, and Midgley (1) [2] isolated these hydrocarbons in a high degree

[1] This work is part of an investigation on the electrical properties of insulating liquids which is being carried on in cooperation with the Utilities Research Commission (Inc.), Chicago, Ill.

[2] The figures in parentheses here and throughout the text relate to the bibliography at the end of this paper.

of purity from petroleum, and have published values for their physical constants which, in general, are in satisfactory agreement with those obtained in this investigation. Since, however, the hydrocarbons obtained in this work were prepared synthetically, a brief description of the methods and a comparison of the values obtained for the physical constants with those of Shepard, Henne, and Midgley (1) seems desirable.

In addition to the hydrocarbons, two of the intermediates in their preparation, *n*-amyl bromide and *n*-nonyl bromide, were obtained in a pure condition and certain of their physical constants measured. Nonyl bromide in particular proved interesting since it was found to exist in two crystalline modifications, a fact not previously recorded.

II. METHODS

The methods used in the purification, in the determination of purity, and in the measurement of the physical constants were similar for all the hydrocarbons and are referred to frequently in discussing the individual substances. It is therefore advisable to describe these methods briefly at this point before proceeding to a more detailed description of the individual syntheses and purifications.

1. PURIFICATION

The physical methods employed were fractional distillation and fractional crystallization. Apparatus and methods for efficiently pursuing these processes have been developed in this bureau, and were used with only minor modifications. The liquids were distilled through a 10-plate bubble cap fractionating column (2, 3) fitted with a variable reflux regulator of the type described by Marshall (4). The reflux ratio during the final distillation was always greater than 10 : 1. The distillation range was read on a thermometer extending into the vapor from the top of the column. The method employed in fractional crystallization (5) was to transfer the frozen material to a vacuum funnel, stir it to a mush, and draw off the mother liquor with suction. For the liquids whose freezing points were higher than that of decane, melting took place so slowly that a vacuum funnel was unnecessary. In the case of decane, the crystals were separated from the mother liquor in a centrifuge designed for use at low temperatures by Hicks-Bruun and Bruun (6).

2. FREEZING POINT DETERMINATIONS

The freezing point determinations were made with a glass-incased, 25.5 ohm (at the ice point), potential terminal, platinum resistance thermometer of the strain-free type, using as accessories a Mueller thermometer bridge and commutator. The thermometer was calibrated by the heat division of this bureau.

The sample was contained in a double-walled Pyrex tube. By varying the air pressure in the annular space of this double walled tube, any desired rate of cooling could be obtained. This vessel was about 11 inches in length and was filled to a depth of 8½ inches with the liquid in question. With the thermometer in place, the liquid extended 4 inches above the resistance coil. The liquid could be stirred vigorously by means of a spiral of nickel chromium wire which

surrounded the thermometer. After the sample (about 70 ml) had been introduced and the thermometer and stirrer adjusted in place, a thin brass tube (as a safety measure) was fitted over the vessel, which was then immersed in liquid air. Freezing took place from the walls toward the center. Stirring was possible until the sample was about half frozen. A change in the slope of the cooling curve was noticed (particularly if the sample was impure) as soon as stirring stopped. This may be explained on the supposition that equilibrium conditions were no longer maintained, and the impurities crystallized simultaneously with the pure substance. The freezing point of any liquid was taken as the temperature at which the cooling curve (figs. 2 to 11) became approximately horizontal. The principal criterion of purity was the slope of this approximately horizontal portion of the freezing point curve.

Considerable precision was attained with these arrangements. Duplicate experiments were made with hexane, octane, decane, and dodecane, and in no instance was a variation greater than 0.002° C. in the freezing point obtained.

An examination was made of the thermometric technique in order to determine how accurately the measured temperatures agreed with the international scale of temperature. The question of conduction through the leads was studied by varying the height of the liquid above the resistance coil. Determinations of the freezing point of hexane in which this height was varied from 5 to 2 inches agreed within 0.001° C., and indicated that with the apparatus in question this effect was negligible. For the thermometer regularly used, the values of the constants given by the heat division of this bureau permitted the calculation of the temperature with an accuracy of 0.02° C. In order to obtain a further test on the accuracy of this thermometer and accessories, freezing-point determinations were made on two samples, using the equipment of the low-temperature laboratory of this bureau, with the assistance of R. B. Scott. The values −56.82° and −95.36° C. obtained on samples of octane and hexane with the equipment of the low-temperature laboratory compare well with the values −56.82° and −95.37°C., which had been obtained on these samples with the regular equipment. Thus with two different thermometers, bridges, and operators the maximum discrepancy was 0.01° C. It seems reasonable to conclude that the thermometric measurements do not differ from the international scale by more than ±0.02° C.

3. BOILING-POINT DETERMINATIONS

The boiling points were determined with the aid of a platinum resistance thermometer in the apparatus shown in Figure 1. Vapor given off from the boiling liquid in the flask had, first, to pass through liquid in the bubble cap before reaching the thermometer, thus preventing superheating. The outer jacket was electrically heated sufficiently to permit the liquids with high boiling points to distill over, but was always kept somewhat below the boiling temperature. About half of the 50 ml sample was distilled over during a boiling-point determination. The temperature generally rose less than 0.01° C. except during the distillation of the first few milliliters when the thermometer was warming up. Barometric pressures within 0.02

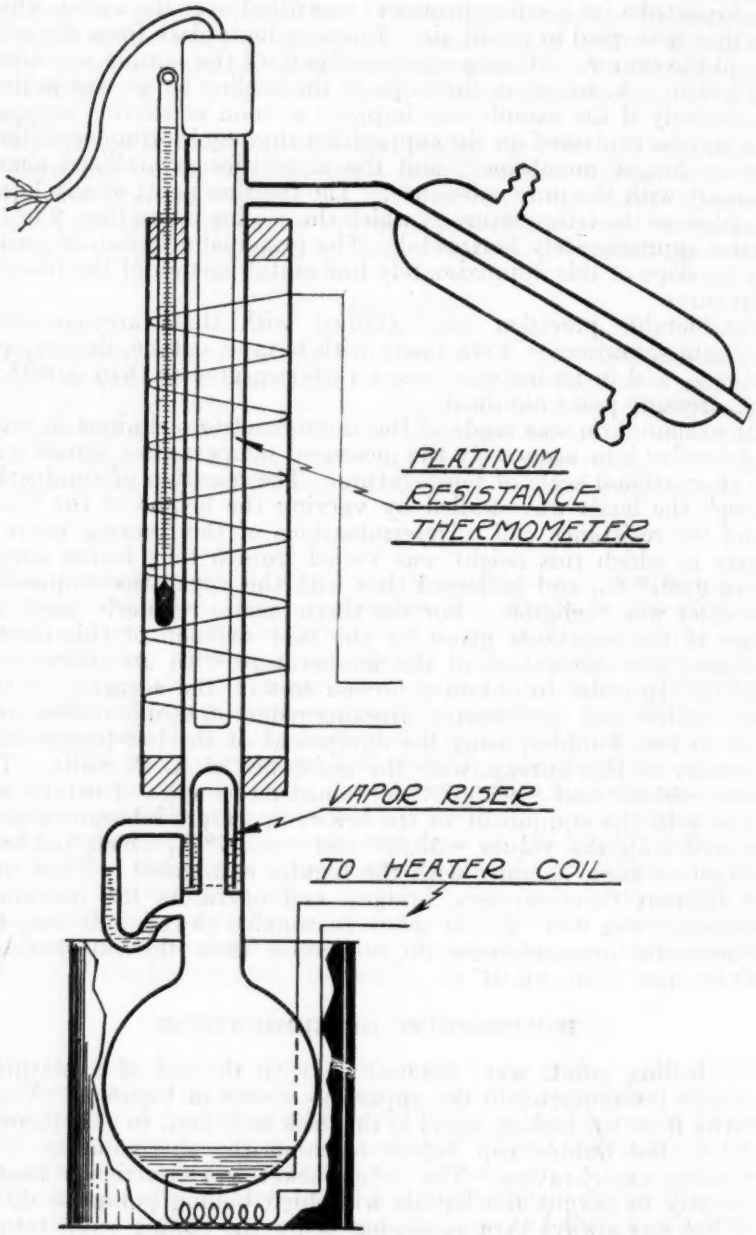

FIGURE 1.—*Boiling-point apparatus*

mm were obtained immediately before and after the boiling-point reading from the aeronautic-instruments section of this bureau. The boiling points of the hydrocarbons were corrected to 760 mm with the aid of the values given by Shepard, Midgley, and Henne (1) for $\frac{dt_B}{dp}$, the rate of change of boiling point with change of pressure. For *n*-amyl bromide several boiling-point determinations in the vicinity of 760 mm were used to compute $\frac{dt_B}{dp}$. Duplicate boiling-point determinations were made in most cases and agreed within 0.01° C.

4. REFRACTIVE INDEX DETERMINATIONS

Refractive indices were measured by L. W. Tilton, of the optical instruments section of this bureau, with three different Abbe refractometers. Each was calibrated with distilled water and with several prismatic standards of refractivity whose indices had been previously measured on a spectrometer by the method of minimum deviation (7). The observations on these liquids were made at water jacket temperatures of 25° C. in a room the temperature of which was between 23° and 24° C. On each instrument two series of measurements were made in which the liquids were sampled in the direct and also in the reverse order of their optical densities. Each of these samplings consisted of two successive applications of liquid to the refractometer block by means of a clean glass rod, and the instruments were set and read twice after each application.

The precision of these refractive index readings is characterized by probable errors of a few units in the fifth decimal place. With instruments so calibrated an accuracy of $\pm 5 \times 10^{-5}$ is attainable when using solid samples. With liquids, however, the accuracy may be affected by contamination of the small samples when they come in contact with the cement which holds the refractometer block in its water jacket. Also, the high volatility of some of the samples of lower index causes them to cool appreciably and, perhaps, to maintain a temperature lower than that indicated by the thermometer which is immersed in the jacketing stream. In accord with this supposition the results on the different refractometers do not agree as well for the liquids having the lower indices. In no case, however, does the index as determined by any one refractometer depart from the mean recorded in Table 1 by more than $\pm 12 \times 10^{-5}$, the average of such departures being $\pm 3 \times 10^{-5}$.

III. SYNTHESIS AND PURIFICATION

The synthesis and purification of the hydrocarbons and some of their intermediate products are described in the following paragraphs.

1. *n*-PENTANE

The Sharples Solvent Corporation, of Philadelphia, kindly supplied a gallon of amyl alcohol for this preparation. This material was stated by them to be a mixture of 2-pentanol and 3-pentanol with not more than 1 per cent of tertiary amyl alcohol and possibly a trace of diamylene. Fractional distillation yielded a large middle fraction

boiling between 116.4° and 118.4° C., which was undoubtedly a mixture of 2 and 3 pentanol. Both of these substances on dehydration and subsequent hydrogenation yield *n*-pentane. The dehydration was performed with the use of sulphuric acid exactly as described in Organic Syntheses (8). The pentenes thus obtained were fractionated and the portion which distilled between 35.8° and 36.4° C. was retained. The pentenes were then hydrogenated by passage through a reaction tube filled with nickel catalyst maintained at 140° C. Practically complete reduction took place in one passage. The re-

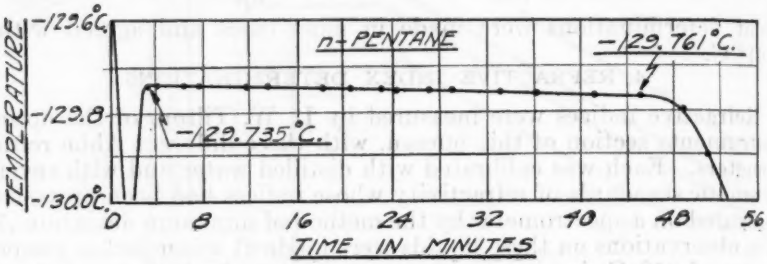

FIGURE 2.—*n-pentane cooling curve*

sulting pentane was shaken three times with concentrated sulphuric acid, then washed twice with a 10 per cent solution of sodium carbonate, and finally with water. After drying with calcium chloride, the pentane was fractionally distilled three times. About 750 ml boiling over a range of 0.03° C. was collected as pure material. An examination of the freezing point curve (fig. 2) indicates the high purity of the sample. The material froze between −129.735° and −129.761° C., a range of 0.026° C.

2. *n*-HEXANE

The starting material in this synthesis was *n*-propyl alcohol. It was converted into the bromide by the hydrobromic-sulphuric acid

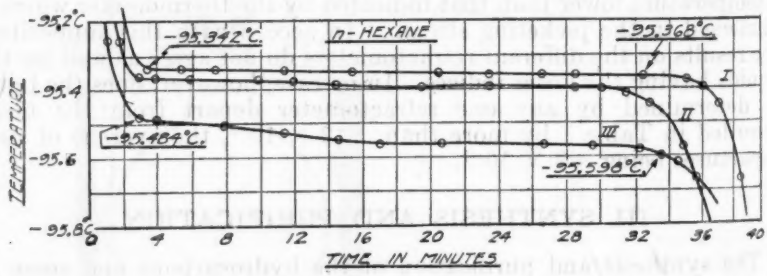

FIGURE 3.—*n-hexane cooling curves*

method (9). The bromide was then converted into hexane by treatment with sodium shot, using the method employed by Faillebin (10). The last traces of *n*-propyl bromide were removed by refluxing the crude hexane with liquid sodium potassium alloy for four hours. The hexane was then shaken with cold concentrated sulphuric acid until the acid layer was colorless, then shaken with a 10 per cent solution

of sodium carbonate, then with water, and finally dried with anhydrous calcium chloride. This material was fractionally distilled thrice, and 1,500 ml which distilled within 0.04° C., was obtained. It was collected in two nearly equal fractions which showed a pronounced difference in freezing behavior, although distilling within 0.04° C. (Fig. 3.) The second fraction (Curve *II*) gave a more nearly horizontal curve and froze 0.12° C. higher than the first fraction. (Curve *III*.) A 400-ml portion of the second fraction was stirred with 175 ml of chlorosulphonic acid at 45° C. for seven hours. (This reagent has been reported as efficacious in the removal of branch chain hydrocarbons (11, 12).) After washing thrice with a 10 per cent solution of sodium hydroxide and once with water, the sample was dried with calcium chloride and again distilled. The freezing range of this sample as shown in Curve *I* (−95.342° to −95.368° C.) was only 0.026° C., and indicated that the hexane was of high purity.

3. *n*-HEPTANE

Several liters of heptane, the original source of which was the Jeffrey pine, was furnished by Graham Edgar, of the Ethyl Gasoline Corporation. This material was of very high purity, as is illustrated

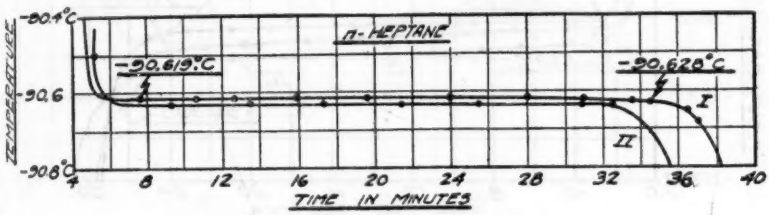

FIGURE 4.—*n-heptane cooling curves*

by its freezing behavior. (Fig. 4, Curve *II*.) Vigorous treatment with chlorosulphonic acid and subsequent distillation raised the freezing point 0.008° C. Curve *I* illustrates the freezing behavior of the treated sample. This sample froze from −90.619° to −90.628° C., a range of only 0.009° C., indicative of exceptionally high purity. The same value, −90.62° C., was obtained on a sample of heptane isolated from petroleum by Hicks-Bruun and Bruun (6).

4. *n*-OCTANE

The starting material in this synthesis was *n*-butyl alcohol. It was converted into the bromide by the hydrobromic-sulphuric acid method (9). The bromide was then converted into octane in a manner similar to that employed by Lewis, Hendricks, and Yohe (13). The procedure was as follows: Sodium in 73 g portions was converted to a finely divided shot by melting and shaking under xylene in a 1-liter 3-necked Pyrex flask. The xylene was decanted and the sodium washed several times with anhydrous ether. It was then covered with 300 ml of anhydrous ether and the flask fitted with a dropping funnel, stirrer with mercury seal, and reflux condenser with calcium chloride tube. The flask was placed in an ice-water bath, the stirrer started, and 384 g of *n*-butyl bromide run in over a period of three hours. The excess sodium was destroyed by running water

into the mixture. The octane layer was drawn off, and the ether and octane separated by fractional distillation. The impure octane was then refluxed with a 10 per cent solution of sodium hydroxide in alcohol for several hours to destroy any unconverted butyl bromide. Water was then added, and the octane separated from the aqueous layer. It was shaken with cold concentrated sulphuric acid until the acid layer remained colorless; then shaken with a 10 per cent solution of sodium carbonate, then with water, and finally dried over calcium chloride. In this way 3,200 ml of crude material was prepared. It was fractionally distilled four times. At the end of this fractionation, 1,800 ml of material distilling within a range of 0.04° C. was obtained. This material was collected in two equal fractions which had the same freezing point. However, judging from the slope of the freezing-point curve (fig. 5, Curve *III*), it was not yet pure. A sample further purified by three fractional crystallizations froze as shown in Curve *II*. This material, although freezing at a higher temperature, still showed almost as great a freezing range.

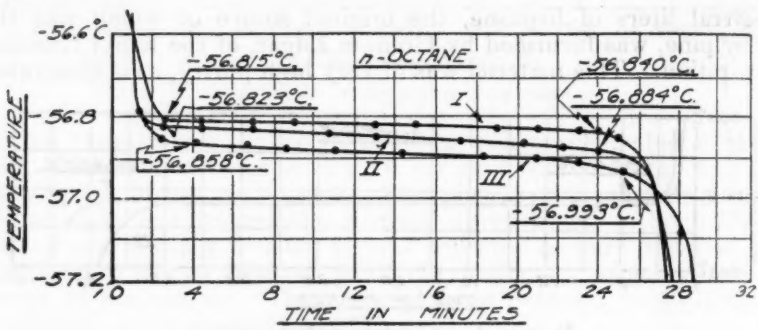

FIGURE 5.—*n-octane cooling curves*

Another sample was stirred with chlorosulphonic acid at 45° C. for seven hours and this treatment repeated with fresh chlorosulphonic acid three times. The octane was separated from the chlorosulphonic acid, washed with a 10 per cent solution of sodium hydroxide, then with water, dried over calcium chloride, and again fractionally distilled. As a result, 270 ml of material was obtained, freezing between −56.815° and −56.840° C., a range of 0.025° C., which indicates its high purity.

5. *n*-NONANE AND *n*-NONYL-BROMIDE

The starting materials in this synthesis were *n*-heptyl bromide and ethylene oxide obtained from Eastman Kodak Co. and from Carbide & Carbon Chemicals Corporation. From these *n*-nonyl alcohol was prepared according to the following reactions:

$$CH_3(CH_2)_5CH_2Br + Mg \longrightarrow CH_3(CH_2)_5CH_2MgBr$$

$$CH_3(CH_2)_5CH_2MgBr + CH_2 - CH_2 \longrightarrow$$
$$\qquad\qquad\qquad\qquad\qquad\quad \diagdown O \diagup$$

$$CH_3(CH_2)_7CH_2OMgBr \xrightarrow{H_2O} CH_3(CH_2)_7CH_2OH$$

This method is exactly analogous to the preparation of *n*-hexyl alcohol from *n*-butyl bromide and ethylene oxide described in Organic Syntheses (14). The *n*-nonyl alcohol was fractionally distilled under a pressure of 83 mm. From the original 1,000 g of *n*-heptyl bromide, 545 ml of *n*-nonyl alcohol distilling between 143.7° and 144° C. was obtained. This purified alcohol was converted into *n*-nonyl bromide by the hydrobromic-sulphuric acid method (9). The resulting product was fractionally distilled at 83 mm and the material distilling between 144.55° and 144.60° C. used in the synthesis of *n*-nonane.

The *n*-nonyl bromide was converted in the usual manner into nonyl magnesium bromide, which was then decomposed with ice and the nonane separated by steam distillation. It was then shaken in turn with concentrated sulphuric acid, 10 per cent sodium carbonate solution, dried over calcium chloride, and fractionally distilled once. A yield of 210 ml of *n*-nonane distilling within a range of 0.03° C. was obtained. The freezing behavior is shown in Figure 6. The freezing range from −53.700° to −53.754° C. was 0.054° C., which is somewhat greater than that obtained for the other hydrocarbons, indicating a less pure material. The freezing point, −53.70° C., is

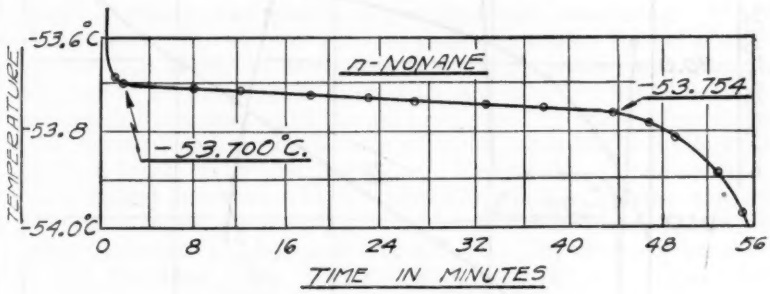

FIGURE 6.—*n-nonane cooling curve*

lower than the value −53.68° C. given by Shepard, Henne, and Midgley (1), and the value −53.65° C. obtained on a sample of very pure nonane isolated by White and Rose (15) from petroleum.

The behavior of *n*-nonyl bromide during its freezing point measurements indicated clearly that two crystalline modifications of this substance exist. Curve *I* (fig. 7) is a time temperature cooling curve obtained in the usual manner with stirring. The temperature, after remaining constant at −30.71° C. for about seven minutes, rose abruptly to −29.06° C., and again remained approximately constant for a short time. Simultaneously with this rapid temperature change, stirring became much easier. If the liquid was not stirred, crystallization occurred at −30.71° C. without the appearance of the β-modification. Curves *II* and *III* are heating curves, Curve *II* showing the behavior of a sample which had been frozen with stirring and in which the β-phase had made its appearance, while Curve *III* shows the behavior of a sample frozen without stirring in which the β-phase had not appeared. These curves show a difference in melting behavior and afford confirmation of the existence of two modifications. The freezing point of the α-modification is −30.71° C. The freezing point of the β-modification can not be stated so definitely, since it is possible that the approximately flat portion of the Curve (*I*) is caused

by an equality between the loss of heat to the surroundings and the gain in heat caused by the transformation. The freezing point of the β-modification, however, can not be below $-29.06°$ C., and judging from the heating Curve (*III*), it seems improbable that it can be appreciably higher. Moreover, in another time-temperature cooling experiment, a horizontal portion of the curve was obtained at $-29.06°$ C. Thus it seems probable that $-29.06°$ C. represents the true freezing temperature of the β-modification.

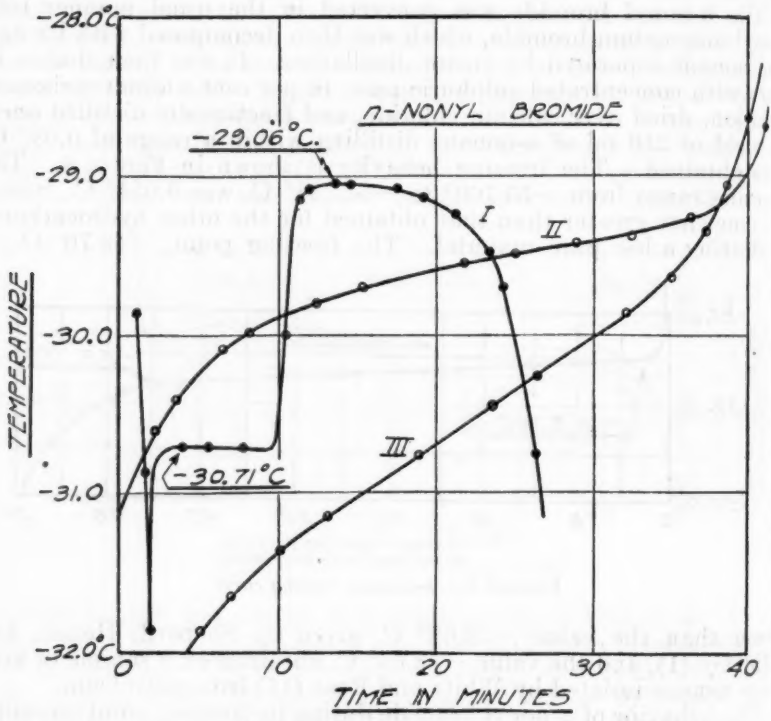

FIGURE 7.—*n-nonyl bromide*

I, cooling curve, *II* and *III* heating curves

6. *n*-DECANE AND *n*-AMYL BROMIDE

The starting material in this synthesis was Eastman's *n*-propyl alcohol. It was converted to *n*-propyl bromide by the hydrobromic-sulphuric acid method (9). The resulting bromide was fractionally distilled once. The bromide was then converted to *n*-amyl alcohol by the use of ethylene oxide in a manner exactly analogous to that of the preparation of *n*-hexyl alcohol from *n*-butyl bromide and ethylene oxide, described in Organic Synthesis (14). The *n*-amyl alcohol was fractionally distilled twice and 1,600 ml of material distilling between 137.82° and 137.92° C. obtained. This was converted to the bromide by the hydrobromic-sulphuric acid method (9) and 1,150 ml of the bromide distilling between 129.40° and 129.50° C. obtained. The freezing range of this material (fig. 8) was only 0.014° C. and

indicated it to be of high purity. This material was used to synthesize decane as follows: Pea-sized sodium pellets were added through a reflux condenser to 100 ml portions of amyl bromide in a 500 ml flask at such a rate that the liquid, which was first heated to boiling, continued to boil gently. After no more sodium could be added (owing to accumulation of solid), the reaction mixture was cooled, treated with water, and the hydrocarbon layer separated and dried with calcium chloride. This process was repeated three times before

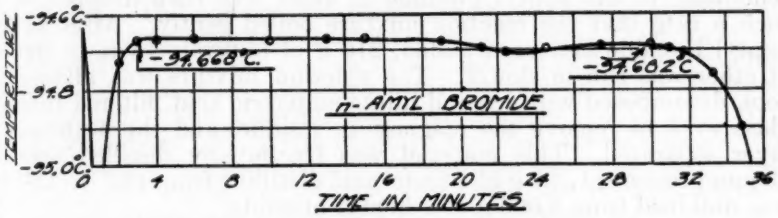

FIGURE 8.—*n-amyl bromide cooling curve*

the amyl bromide was practically completely converted. Finally the decane was refluxed over sodium potassium alloy for six hours to remove the last traces of amyl bromide. The decane was decanted from the alloy and shaken in turn with several portions of cold concentrated sulphuric acid until the acid remained colorless, then shaken with 10 per cent sodium carbonate solution, and finally with water. It was then fractionally distilled once. Practically all the sample of 505 ml distilled between 173.37° and 173.47° C. It was collected in two nearly equal fractions, one between 173.37° and 173.43° C., the other between 173.43° and 173 47° C. The freezing points of these two fractions were −29.88° and −29.76° C., respectively.

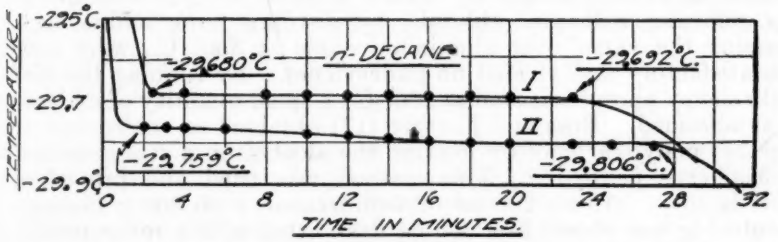

FIGURE 9.—*n-decane cooling curves*

The cooling curve for the sample which gave −29.76° C. as the freezing point is shown in Figure 9 (Curve *II*). Shortly after this sample was obtained Bruun and Hicks-Bruun (16) obtained from petroleum by distillation and by crystallization, with the use of a centrifuge, a decane sample of exceptional purity freezing at −29.68° C. By fractional crystallization with the same centrifuge, the freezing point of the synthetic sample was raised to the identical value −29.68° C. The freezing range from −29.680° to −29.692° C. (Curve *I*, fig. 9) indicates very high purity.

7. *n*-UNDECANE

The starting materials in this synthesis were Eastman's best grade of *n*-heptyl bromide and *n*-butyraldehyde from which 4-undecanol was synthesized as follows: A 50 ml portion of a mixture of 537 g of *n*-heptyl bromide in 900 ml of anhydrous ether was run onto 75 g of magnesium in a 5-liter 3-necked flask, fitted with reflux condenser, stirrer with mercury seal, and dropping funnel. A crystal of iodine was added and the reaction started by warming slightly. The remainder of the heptyl bromide in ether was then dropped in at such a rate that the reaction mixture boiled gently. After all the heptyl bromide had been added, 216 g of butyraldehyde in 200 ml of ether was run in slowly. The reaction mixture was allowed to cool, decomposed with ice and dilute sulphuric acid, filtered through glass wool to remove the magnesium residue, and the 4-undecanol layer separated. This material was fractionally distilled once at 93 mm pressure; 1,230 g of 4-undecanol distilling from 155° to 157° C. was obtained from 3,000 g of *n*-heptyl bromide.

The dehydration of 4-undecanol should yield a mixture of two undecylenes, depending on the manner in which water splits off. Thus

$$C_2H_5\cdot\underset{\boxed{H}}{CH}\cdot\underset{\boxed{OH}}{CH}\cdot CH_2\cdot C_6H_{13}\rightarrow C_2H_5\cdot CH=CH\cdot CH_2\cdot C_6H_{13}$$

or

$$C_2H_5\cdot CH_2\cdot\underset{\boxed{OH}}{CH}\cdot\underset{\boxed{H}}{CH}\cdot C_6H_{13}\rightarrow C_2H_5\cdot CH_2\cdot CH=CH\cdot C_6H_{13}$$

Both of these undecylenes should yield *n*-undecane on hydrogenation.

However, the dehydration of 4-undecanol proved to be difficult. Attempts to dehydrate it by heating with 60 per cent sulphuric acid, by refluxing with zinc chloride, by distilling from iodine, and by passing the vapor over aluminium oxide at 350° C., were entirely unsatisfactory and yielded no undecylenes. By running the alcohol into sirupy phosphoric acid at 250° C., a small quantity of undecylene was obtained. Ross and Leather (17) obtained an undecylene from methyl nonyl carbinol by heating the alcohol on a steam bath with phosphorus pentoxide. This method was tried and proved more satisfactory. About 200 ml of 4-undecanol, with 100 g phosphorus pentoxide was placed in a 500-ml flask fitted with a reflux condenser and calcium chloride tube. The flask was then heated for eight hours on a steam bath. The resulting pasty material was extracted with ether and the extract fractionally distilled. In addition to the undecylenes distilling from 191° to 193° C., a considerable quantity of material (almost half) distilled in the range from 222° to 223° C. This material gave the phenylhydrazine test for a ketone. It was probably propyl heptyl ketone and resulted from the oxidizing action of phosphorus pentoxide. This ketone was reduced to 4-undecanol by mixing with an equal volume of amyl alcohol, and adding an excess of sodium in small pieces to the boiling mixture. It was then washed with water, dried, and separated from the amyl alcohol by fractional distillation. It distilled at atmospheric pressure from 228° to 229° C. The 4-undecanol thus obtained was treated with phosphorus pentoxide

as before and more undecylene obtained. Altogether 800 ml of undecylene was obtained from 1,230 g of 4-undecanol.

Attempts to hydrogenate the undecylene to undecane by passage over a nickel catalyst at 200° C. were not satisfactory. The first small portion which was collected was almost completely hydrogenated, but the catalyst soon became inactive, presumably owing to poisoning by impurities in the undecylene. The undecylene was, however, satisfactorily hydrogenated by passage over a copper chromite catalyst (18) at 200° C., this catalyst being less readily poisoned than nickel. The undecylenes remaining unconverted were removed by shaking with cold concentrated sulphuric acid. The undecane was washed with a 10 per cent solution of sodium carbonate and dried with calcium chloride. Approximately 700 ml of crude undecane was obtained. This material was quite impure. After four fractional distillations 350 ml was obtained distilling over a range of 0.5° C. Freezing point measurements showed that this material was still quite impure. Fractional crystallization was used for final purification and the progress of purification followed with the platinum resistance thermometer. After many fractional crystallizations 75 ml of

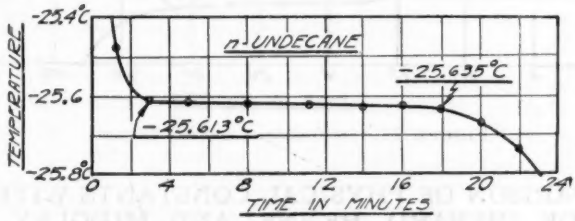

FIGURE 10.—*n-undecane cooling curve*

very pure material was obtained, 75 ml only slightly less pure, and 100 ml of fairly pure material. The freezing range of the purest sample, from −25.613° to −25.635° C., was only 0.022° C. and is indicative of high purity. (Fig 10.)

8. *n*-DODECANE

The starting materials in this synthesis were *n*-butyl bromide and ethylene oxide from which hexyl alcohol was synthesized as described in Organic Syntheses (14). The hexyl alcohol resulting was fractionally distilled and the portion distilling between 156° and 157° C. converted into the bromide by the hydrobromic-sulphuric acid method (9). Practically all of this hexyl bromide distilled between 155.20° and 155.32° C.

Dodecane was prepared from the hexyl bromide by the use of sodium in exactly the same manner as decane from amyl bromide. Finally the dodecane was refluxed over sodium potassium alloy for six hours to remove the last traces of hexyl bromide. The dodecane was then decanted from the alloy and shaken with several portions of cold concentrated sulphuric acid until the acid remained colorless, then shaken with a 10 per cent solution of sodium carbonate and finally with water. Two fractional distillations at atmospheric pressure yielded 570 ml of dodecane with a distilling range of 0.2°. It had a slightly acrid odor, and evidently contained unsaturated compounds

caused by cracking at the high temperature necessary to distill at atmospheric pressure. Its freezing behavior indicated that it was not pure. (Fig. 11, Curve *II*.) After many crystallizations, a 75 ml sample with the freezing behavior shown in Curve *I* was obtained. This material froze from −9.609° to −9.669°, a range of 0.06° C., indicative of a fairly pure material, through probably not as pure as some of the other hydrocarbons obtained.

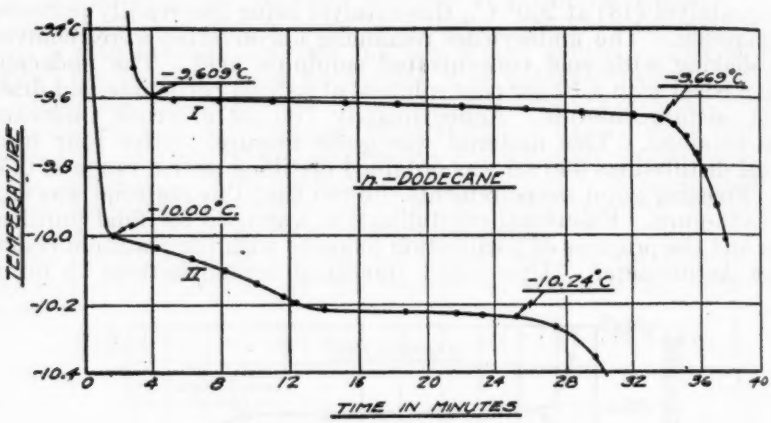

FIGURE 11.—*n-dodecane cooling curves*

IV. COMPARISON OF PHYSICAL CONSTANTS WITH THOSE OF SHEPARD, HENNE, AND MIDGLEY

Physical constants of all the hydrocarbons described in this paper are available in the literature. In general, the criteria of purity were not as strict as those employed in this investigation and the methods of determining the constants, in particular the methods of determining temperature, were not sufficiently refined to yield results of high accuracy. In consequence, the freezing points reported in the literature differ widely. The values obtained on samples isolated from petroleum at this bureau, to which reference has already been made (6, 15, 16) and the values obtained by Shepard, Henne, and Midgley (1) are notable exceptions to this statement. Only Shepard, Henne, and Midgley (1) have recorded values for the entire series from pentane to dodecane. Their values, moreover, were obtained on samples isolated from petroleum, so that a comparison with values on samples obtained in an entirely different manner; that is, by synthesis, is valuable in establishing the true value of the constants. For these reasons only the values of Shepard, Henne, and Midgley (1) are recorded for comparison in Table 1.

TABLE 1.—*Physical constants of normal hydrocarbons*

Substance	Boiling point at 760 mm [1]		Freezing point in air		Refractive index N_D^{25}	
	Author	Shepard, Henne, and Midgley	Author	Shepard, Henne, and Midgley	Author	Shepard Henne, and Midgley
	°C.	°C.	°C.	°C.	°C.	°C.
Pentane	36.06	36.00	−129.73	−129.93	1.35470	1.35495
Hexane	68.70	68.71	−95.34	−95.39	1.37224	1.37230
Heptane	98.38	98.38	−90.62	−90.65 −90.62 [3]	1.38510	1.38553
Octane	125.59	125.59	−56.82	−56.90	1.39509	1.39534
Nonane	150.72	150.71	−53.70	−53.68 −53.65 [3]	1.40318	1.40340
Decane	174.02	174.06	−29.68	−29.76 −29.68 [3]	1.40961	1.40986
Undecane [2]			−25.61	−25.65	1.41495	1.41516
Dodecane [2]			−9.61	−9.73	1.41952	1.41967
Amyl bromide	129.58		−94.67		1.44199	
α-Nonyl bromide			−30.71		1.45221	
β-Nonyl bromide			−29.06		1.45221	

[1] The values for dt_B/dp for the hydrocarbons were taken from the paper by Shepard, Henne, and Midgley (1) while that for amyl bromide was determined and found equal to 0.048° /mm.
[2] The boiling point of undecane and dodecane and *n*-nonyl bromide were not determined owing to the probability of some thermal decomposition.
[3] Values obtained on samples isolated from petroleum by Hicks-Bruun and Bruun (6) (heptane), White and Rose (15) (nonane), and Bruun and Hicks-Brunn (16) (decane).

The agreement between these two sets of values of physical constants, although somewhat less satisfactory than is to be desired, is nevertheless much superior to that generally obtained by investigators on the physical constants of organic liquids. The greatest discrepancy occurs with pentane in which there is a difference of 0.06° in the boiling point and 0.2° in the freezing point. The agreement on the boiling points from hexane to nonane is excellent. The freezing point agreement is not so satisfactory. With the exception of nonane (which was not quite pure), the freezing point values obtained in this work are all higher than those obtained by Shepard, Henne, and Midgley (1). It is probable that the higher values should be considered the more reliable since impurities, except with one type of solid solution, lower the freezing point. Dodecane, as shown by the slope of the freezing point curve, was not quite pure, and it seems possible that the true freezing point may be still higher than the value recorded here, by from 0.05° to 0.1° C. Unfortunately, sufficient dodecane was not available to continue the fractional crystallization and test this point. The other hydrocarbons were purer than nonane and dodecane and their freezing points are probably correct within 0.02° to 0.05° C.

The values recorded here for the refractive indices are lower than those given by Shepard, Henne, and Midgley (1). The average value of the differences is 22×10^{-5}.

Refractive indices are not a sensitive test for small amounts of impurities, particularly if the refractive index of the impurity is close to that of the pure substance. Thus 1 per cent of heptane in 99 per cent of octane with refractive indices of 1.38510 and 1.39509, respectively, would give a liquid with refractive index of 1.39499, differing by only 10×10^{-5} from that of pure octane. A calculation based on the differences between the freezing point values given by Shepard, Henne, and Midgley (1), and those recorded here, shows

that the difference in purity is generally much less than 1 mole per cent. Since the impurities most likely to be present in both cases are isomers, the refractive indices of which do not differ greatly from those of the normal hydrocarbons, it is improbable that the average value for the difference, 22×10^{-5}, can be accounted for by impurities, but instead is attributable to differences in the instruments or methods of measurement.

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WASHINGTON, March 11, 1932.

A STUDY OF SOME CERAMIC BODIES OF LOW ABSORPTION MATURING AT TEMPERATURES BELOW 1,000° C.

By R. F. Geller and D. N. Evans

ABSTRACT

This paper contains a report of an investigation involving the development and testing of a number of ceramic bodies of the whiteware type containing synthetic flux and maturing below 1,000° C. The bodies compare favorably in transverse breaking strength with earthenware, are nearly white in color and vary in absorption from 1 to 5 per cent. The resistance to mechanical abrasion is higher than that of nonceramic flooring materials, such as marble. Glazed specimens resisted crazing satisfactorily in laboratory tests.

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I. INTRODUCTION

The idea of using artificially prepared fluxing agents in ceramic bodies to produce structures, having desirable strength and porosity, at temperatures below those required by the feldspathic fluxes is not new.[1] According to the Encyclopædia Britannica this idea had its inception not later than 1581, when a factory was established at Florence under the patronage of Francesco de Medici to produce white porcelain by introducing common glass into the body. The manufacture was continued at Pisa, and similar porcelain is attributed to Candiana near Padua. Another factory, founded at St. Cloud,

[1] Encyclopædia Britannica, vol. 18, 14th ed., p. 351, which refers to "Pottery and Porcelain, A Handbook for Collectors." Vol. III, E. Hannover (Ed. B. Lockham). A. B. Searle, Encyclopædia of Ceramic Industries, vol. 2, p. 377.

had grown to considerable size by the end of the seventeenth century. Searle states that porcelains, heated at low temperatures and made translucent by the aid of especially prepared glassy mixtures of frit were first produced at St. Cloud in 1727 and at Vincennes in 1740. These porcelains are now known as Pate Tendre or soft paste and are matured at temperatures above 1,000° C.[2] The same idea has been applied in more recent times to the manufacture of a type of ware named belleek, presumably after Belleek in County Fermanagh, Ireland.

The last few years have witnessed a renewed interest in the use of artificially prepared fluxes. With the development of methods for utilizing the electric current as a means for producing controlled temperatures, there naturally arises the question of the possibility of adapting this source of heat to the maturing of ceramic whiteware. It has been proven practicable to heat some classes of whiteware by passing the electric current through nonmetallic resistors. However, it would be an added economy and convenience if bodies of satisfactory qualities could be matured at, or below, 1,000° C. and consequently in furnaces of the metallic resistor type. The information contained in the literature [3] is lacking in specific data, particularly with reference to bodies produced at temperatures below 1,000° C. Moreover the field covered by the patent literature referred to is in general that of earthenware.

It was therefore the purpose of this investigation to determine the properties of a limited number of bodies having low absorptions and maturing below 1,000° C., and to obtain results serving as a guide to future industrial developments.

[2] Temperatures are expressed in degrees Centigrade throughout this report.

[3] German Patent No. 182107 (Mar. 19, 1907); British Patents Nos. 253184 (June 9, 1926), 302519 (Dec. 20, 1928), 318188 (Aug. 30, 1929), and 323379 (Jan. 2, 1930); U. S. Patents Nos. 1749642 (Mar. 4, 1930), Re. 17530 (May 6, 1930) and 1819686 (Aug. 18, 1931). Also, P. F. Collins, J. Am. Cer. Soc., vol. 11 (9), p. 706, 1928, and vol. 15 (1), p. 17, 1932.

TABLE 1.—*Compositions of frits, given in molecular proportions*

TABLE 1.—*Compositions of fluxes, given in molecular proportions*

Flux No.	Na_2O	MgO	SrO	ZnO	CaO	Al_2O_3	B_2O_3	Sb_2O_3	P_2O_5	SiO_2	ZrO_2	F	Remarks
	(RO=1.0)					(R_2O_3=1.3)				(RO_2=1.7)			
[1]1	1.0						1.3			1.7			Fuses readily, pours easily; glass colorless.
2	.8	0.2					1.3			1.7			Same as No. 1.
3	.6	.4					1.3			1.7			Fuses more readily than Nos. 1 and 2, pours easily; glass colorless.
4	.8	.2				0.1	1.2			1.7			Tendency to foam during melting, melts and pours less readily than No. 1; glass clear light yellow (light blue when melted in platinum).
5	.8	.2				.2	1.1			1.7			Tendency to foam greater than No. 4; otherwise similar.
6	.95		0.05				1.3			1.7			Fuses readily, pours easily; glass clear to very light yellow.
7	.95		.05			.2	1.1			1.7			Tendency to foam, melts and pours similar to No. 5. Color clear to light yellow.
8	.9		.1			.2	1.1			1.7			Melts and pours similar to No. 4; glass clear yellow (clear light blue when melted in platinum).
9	.8			0.2			1.3			1.7			Tendency to foam but melts and pours readily; glass colorless.
10	.5			.5			1.3			1.7			Melts and pours less readily than No. 9, otherwise similar.
11	.2			.8			1.3			1.7			Melts fairly readily to a white viscous glass; sample melted in platinum shows small amounts of doubly refracting crystals.
12				1.0			1.3			1.7			More difficult to melt but less opaque than No. 11. Too viscous to pour. Melt consisted of nearly pure glass of index 1.505.
13				1.0		.3	1.0			1.7			More refractory than No. 12; no satisfactory melts obtained of either Nos. 12, 13, or 14.
14				1.0			1.0	0.3		1.7			Did not fuse completely. Evidence of the reduction of zinc, also volatilization of ZnO or Sb_2O_3, or both.
15	.9	.05	.05				1.3			1.7			Fuses and pours readily, glass colorless.
16	.9	.05	.05			.2	1.1			1.7			Same as No. 15, except for tendency to foam during melting.
17	.8	.2					1.3			1.2	0.5		Same as No. 15, except that sample melted in platinum was a clear light yellow.
18	1.0						1.3			1.2	.5		Same as No. 15, except amber in color; sample melted in platinum was clear greenish yellow.
19	.85				0.15		1.3			1.4		0.3	Less fusible than No. 15, but pours satisfactorily; glass clear light yellow.
20	1.0					.3	1.0			1.4		.3	Tendency to foam, fuses fairly readily; glass clear light yellow.
21	.6	.4				.05	1.25			1.4		.3	Melts and pours readily; glass clear amber.
22	.9		.1			.05	1.25			1.4		.3	Foams during melting; fuses with difficulty; glass clear with bluish tinge.
23	.5			.5		.05	1.25			1.4		.3	Fuses and pours satisfactorily although more viscous than Nos. 19 to 22, inclusive; glass clear with bluish tinge.
24	.8				.2		1.2		0.1	1.7			Very refractory and unsatisfactory as a frit; quenched mass composed principally of glass of index 1.515 to 1.522 and 4 to 5 per cent of very fine crystals.
25	1.0					.3	1.0			1.7			Fuses fairly readily, pours easily, no foaming; glass clear with tinge of yellow.
26	1.0					.6	.7			1.7			Considerable foaming during fusion, more refractory than No. 25 and does not pour readily; glass clear greenish yellow.
27	1.0					.8	.5			1.7			Could not be melted satisfactorily.
28	1.0					.45	.85			1.7			Tendency to foam, easier to fuse and pour than No. 26; glass clear with yellow tinge.

[1] Flux No. 1 is of the same composition as flux No. 24 in Auxiliary Fluxes in Ceramic Bodies, by P. F. Collins, J. Am. Cer. Soc. vol. 15 (1), p. 17, January, 1932.

II. MATERIALS

The following materials were used in preparing the artificial fluxes (Table 1): Borax, boracic acid, hydrous magnesium carbonate, zinc oxide, zirconium oxide, fluorspar, cryolite, antimony oxide, potters' flint, and kaolin from Georgia, all of commercial grade; also, sodium nitrate, strontium nitrate, strontium carbonate, and calcium phosphate, all of reagent quality.

The bodies (Table 2) were composed of two or more of the following materials in addition to one of the fluxes: Kaolin from Georgia, ball clay from Tennessee, feldspar containing approximately 50 per cent plagioclase feldspar, 40 per cent potash feldspar and 10 per cent quartz, and artificial "mullite" which was an electric furnace product containing approximately 65 per cent mullite, 12 per cent corundum, and 23 per cent glass. A commercial "soda-lime-silica" bottle glass, ground to pass a No. 100 sieve,[4] was substituted as the flux in one body having the type composition of the "BM Series."

All of the materials used in preparing the glaze (Table 2) were of commercial grade as regularly supplied to the pottery trade.

TABLE 2.—*Compositions of bodies and glaze used in the final series of tests*

A. BODIES[1]

	Series—			
	B	K	BM	KM
	Per cent	*Per cent*	*Per cent*	*Per cent*
Flux	25	25	25	25
Feldspar	35	35	35	35
Ball clay	40	20	35	17½
Kaolin		20		17½
Mullite			5	5

B. GLAZE

Fritt		Glaze[1]	
	Per cent		*Per cent*
Borax	10.3	Fritt	54.4
Boric acid	27.8	Whiting	4.8
White lead	24.3	White lead	16.5
Flint	37.6	Kaolin	24.3

[1] Body compositions are identified by a number followed by the series designation. Thus, 10 BM denotes a body of Series BM in which flux No. 10 was used.

[2] The coefficient of linear thermal expansion (calculated by means of factors in "The Influence of Chemical Composition on the Physical Properties of Glazes," by F. P. Hall, J. Am. Cer. Soc., vol. 13 (3), p.182, 1930) is 5.9×10^{-6}.

III. METHODS

The fluxes were melted in clay crucibles using a gas-fired pot furnace and, when molten, were poured into water, dried, and dry ground to pass a No. 100 sieve. The crucibles held from 1½ to 2 kg of the molten flux and a different crucible was used for each flux.

Relative solubility of the fluxes was determined on specimens obtained by dry sieving a portion of each flux through No. 200 and

[4] Sieves manufactured to meet the requirements of the United States Standard Sieve Series were used throughout this investigation.

No. 270 sieves, using 10 g of that portion which passed the No. 200 and was retained on the No. 270. The specimen was placed in a glass container, together with 200 ml of distilled water, agitated for 48 hours, the liquid removed by filtering, and the residue dried and weighed.

Thermal expansions and "softening temperatures" of the fluxes were determined by the interferometer method [5] on samples of flux which were remelted in platinum, cooled rapidly, and then annealed by heating to their annealing temperatures at an average rate of 2^5 per minute and holding them at these temperatures for one hour and cooling slowly with the furnace. The "softening temperature" was taken arbitrarily as that temperature at which contraction due to softening began to exceed the expansion due to temperature increase.

Indices of refraction of the fluxes were determined by the Becke method.[6]

The bodies were prepared by wet grinding the constituents in a ball mill for two hours, passing them over a magnetic separator and through a No. 100 sieve, and partly drying on plaster. This procedure, and the compositions used, were established after preliminary trials in which various compositions, modifications of wet and dry grinding, addition of flux before and after grinding, and filter pressing were tried.

Specimens for measuring transverse strength, linear shrinkage, and absorption were prepared by kneading the partly dried bodies and extruding them as rods one-half inch in diameter which were cut into 6-inch lengths. The rods were heated to about 750° C. overnight in an electrically heated furnace and matured the next day. Transverse strength is expressed as the modulus of rupture and was calculated from values obtained by breaking the rods across a 5-inch span. Percentage water absorption (which is proportional to porosity) was calculated from the weights of the specimens after having been dried at 115° ± 5° C. and after having been saturated by immersing in water and "autoclaving" for five hours at a steam pressure of 150 lbs./in.^{2}. Linear shrinkage of the rods was determined by measuring the distance, after the heating, between two gage marks which had been pressed 10 cm apart into the freshly extruded rods.

Additional extruded and dried rods were later reground, moistened with about 10 per cent water, passed through a No. 35 sieve, and used in making tile (mold $2\frac{7}{32}$ inches square) and plates (mold 3 inches in diameter) by the "dry-press" method. Total pressure used for both tile and plates was 12,000 pounds. The tile and plates were heated to about 750° C. overnight, in an electrically heated furnace, and matured the next day. Linear shrinkage, absorption, and relative resistance to abrasion of the dry pressed tile were determined on unglazed tile. Linear shrinkage was calculated from the dimensions of the steel mold and of the finished tile. Absorption was determined by the same method used for the extruded rods. Resistance to abrasion, a purely relative value expressed as the H_a value, was obtained by using the apparatus and method of calculation devised by D. W. Kessler [7] for wear tests of flooring materials. Glazed tile and glazed

[5] C. G. Peters and C. H. Cragoe, B. S. Sci. Paper No. 393.
[6] E. S. Larson, U. S. Geological Survey Bulletin No. 679, p. 14, 1921.
[7] A. S. T. M. Proc., vol. 28, Pt. II, p. 855, 1928.

plates were "autoclaved" in water for one and one-half hours at 150 lbs./in.^{2} steam pressure and the number of specimens crazed as a result of this treatment was noted. The "translucency" of a glazed plate was estimated by comparing the intensity of the light it transmitted with that transmitted by an arbitrarily chosen plate of medium "translucency," when such plates were placed over a 2½-inch diameter opening in a box which contained a 75-watt electric light, the filament of which was as near to the opening as possible. The glazed plates were between 3½ and 4 mm in thickness.

TABLE 3.—*Some physical properties of the fluxes*

Flux No.	Solubility		Softening temperature±10° C. Annealed [2]	Index of refraction	Coefficient of linear thermal expansion.[3] Annealed [2]	Flux No.	Solubility		Softening temperature±10° C. Annealed [2]	Index of refraction	Coefficient of linear thermal expansion.[3] Annealed [2]
	A [1]	B [1]					A [1]	B [1]			
	g	*g*	°C.		×10^{-6}		*g*	*g*	°C.		×10^{-6}
1	26	28	535	1.524	11.8	16	7	8	545	1.525	11.0
2	21	22	540	1.514	11.0	17	17	17	530	1.536	10.1
3	11	11	545	1.516	9.4	18	25	28	525	1.538	11.2
4	16	18	540	1.515	10.4	19	12	11	515	1.526	11.7
5	8	8	540	1.523	10.6	20	21	21	490	1.504	12.3
6	15	15	540	1.527	11.2	21	17	17	500	1.506	10.0
7	7	10	545	1.517	11.4	22	16	17	510	1.515	12.1
8	5	6	540	1.522	11.2	23	15	16	480	1.519	9.1
9	24	24	530	1.527	10.9	25	10	11	525	1.524	11.5
10	15	15	525	1.526	8.0	26	1	2	535	1.516	11.6
11	5	6	540	1.529	5.4	28	-------	2	545	1.515	11.1
15	14	13	535	1.524	10.7						

[1] A and B are duplicate determinations calculated on the basis of using 50 g of flux per liter of water.
[2] Fluxes Nos. 20, 21, 22, and 23 were annealed at 475° C., all others at 515° C.
[3] Average coefficient for the temperature range from room temperature to the lower critical temperature. For further information on the "critical temperatures" noted in studies of the thermal expansion of glass see the reference given in Footnote 5. Values to be multiplied by 10^{-6}.

IV. RESULTS

1. FLUXES

A brief description of the melting behavior of the fluxes and their appearance after quenching is given in Table 1. Flux No. 1 is of the same composition as flux No. 24 in the series investigated by Collins [8] and was selected as having a melting point and water solubility justifying its use as a basis on which to build the series of fluxes for this investigation. In outlining the series it is evident that no attempt was made to exhaust the field of possibilities.

Six of the twenty-eight fluxes (Nos. 3, 4, 7, 10, 11, and 28) were selected for intensive study. This choice was based on the observed melting behavior, the physical properties given in Table 3, and the unreported results obtained in a preliminary study. The compositions of the six selected fluxes as determined by calculations based on the batch materials, and by chemical analysis, are given in Table 4. The physical properties determined are presented in Table 5.

Although no specific tests were made of abrasives bonded with the fluxes investigated, it is believed, from observation, that at least some

[8] J. Am. Cer. Soc., vol. 15 (1), p. 17, January, 1932.

of the fluxes have possibilities as bonds for certain classes of manufactured abrasive wheels.

TABLE 4.—*Chemical composition* [1] *of fluxes Nos. 3, 4, 7, 10, 11, and 28*

Flux No. and method	SiO_2	Al_2O_3	CaO	MgO	Na_2O	B_2O_3	ZnO	SrO	Loss on ignition
	Per cent	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*	*Per cent*
3A [2]	37.6	0.42	0.09	5.1	16.7	41.0	------	------	0.31
3C [3]	41.5	------	------	6.5	15.1	36.8	------	------	------
4A	38.8	3.9	.08	3.1	19.5	32.9	------	------	.22
4C	40.3	4.0	------	3.2	19.5	33.0	------	------	------
7A	35.0	7.4	------	.13	24.1	32.3	------	1.8	.32
7C	38.8	7.7	------	------	22.4	29.1	------	1.9	------
10A	37.8	.42	.05	.03	12.2	35.3	14.9	------	.23
10C	38.6	------	------	------	11.7	34.3	15.4	------	------
11A	38.5	.53	.02	.02	4.8	33.7	23.6	------	.34
11C	37.8	------	------	------	4.6	33.5	24.1	------	------
28A	36.6	17.4	.07	.12	23.6	22.1	------	------	.20
28C	38.0	17.0	------	------	23.0	22.0	------	------	------

[1] The chemical analyses were made by J. F. Klekotka and are based on samples dried at 110° C.
[2] Compositions determined by chemical analysis (A).
[3] Calculated compositions based on batch materials (C).

2. BODIES

(a) PRELIMINARY STUDY

The results of this study are not presented in detail, but may be summarized briefly as follows:

Either a dry grinding of all of the constituents, or the addition of the flux after the other constituents of the body have been wet ground, produced coarse textured bodies.

Wet grinding four hours or more introduced so much dissolved flux into the slip that both the slip and the body were unworkable.

Sufficient flux was dissolved during two hours wet grinding to make filter pressing difficult.

Filter cakes contained sufficient water to carry flux to the surface, resulting in the formation of a hard, discolored "skin." (It is suggested that excess water could be removed from these bodies most efficiently by means of spray driers or drum driers.)

No method was found for preparing bodies which could be "jiggered" successfully. Such faulty specimens as were made contained sufficient water to carry dissolved flux to the surface during the drying.

Casting slips made with bodies containing fluxes 3 and 10 worked well on a laboratory scale and thin-walled pieces could be cast without difficulty. Fluxes Nos. 4, 7, 8, 11, and 28 were fairly satisfactory, while others, notably Nos. 1, 16, and 20, produced slips entirely unsuited for casting. However, rapid disintegration of molds was observed with all of the body slips because of the crystallization of dissolved flux carried into them by water from the slip. It was noted that pH values of the slips when removed from the ball mills could not be used as indicators of casting properties in so far as the particular bodies studied are concerned. Slips of bodies containing flux No. 10 showed the lowest pH values determined (approximately 6.0), while the slips containing flux No. 3 showed the highest (approxi-

mately 8.5). McDowell[9] states the pH value at which maximum dispersion is attained is different for each clay and for each electrolyte.

TABLE 5.—*Some physical properties of the fluxes used in the final series of tests as determined by calculation* [1]

Flux No.	Tensile strength	Modulus of elasticity	Coefficient of thermal expansion [2]	
			Calculated	Observed [3]
	kg/mm [2]	*kg/mm* [2]		
3	31.7	6,400	8.6	9.4
4	31.8	6,100	10.3	10.4
7	28.9	5,700	11.6	11.4
10	26.8	7,200	8.6	8.0
11	26.4	7,600	6.6	5.4
28	30.6	6,500	11.9	11.1

[1] Calculations based on the information contained in the reference given in the footnote to Table 2.
[2] Values to be multiplied by 10^{-6}.
[3] Values taken from Table 3.

No difficulty was experienced in making satisfactory specimens of tile and plates by the dry-press process.

Specimens made with 75 per cent flint and 25 per cent flux, when heated to 1,000° C., were translucent, bluish white in color, and of good texture, but the percentage tridymite developed was very high and the specimens were correspondingly sensitive to temperature change in the region of the α-β_1-β_2 tridymite transformations (117° and 163° C.).[10] The average coefficient of expansion for the temperature interval 100° to 200° C. was 41×10^{-6}.

Specimens made with various ratios of feldspar and flux formed highly translucent bodies, but the indicated maturing range did not exceed 10°.

A large majority of the trials indicated that additions of kaolin at the expense of ball clay darkened the color of the product.

Care must be observed in heating to allow ample time between 650° and 750° C. for complete combustion of organic matter before there is appreciable fusion of the flux and consequent sealing of the pores.

Holding at the maximum temperature for not less than one and one-half hours appears to permit the flux to distribute itself more uniformly throughout the body and produce a "smoother" appearing texture.

Specimens in which a commercial bottle glass had been used as a flux, and which had been heated at 990° ± 5° C., had an average absorption of 11.5 per cent. This indicates that commercial bottle glass would probably be unsuitable as a flux for bodies designed to mature below 1,000° C., and which are designed to have relatively low absorptions.

(b) PROPERTIES OF EXTRUDED BARS

The six fluxes selected for more intensive study were used in four series of bodies (Table 2) which have been labeled B, BM, K, and KM.

[9] J. Am. Cer. Soc., vol. 10 (4), p. 225, April, 1927.
[10] C. N. Fenner, Am. J. Sci., vol. 36, p. 331, 1913.

Although it was found that specimens could not be formed successfully from the plastic bodies by jiggering, it was thought advisable to obtain approximate results for their maturing range and other properties by means of conventional tests on extruded bars. Results were obtained for the B and BM series and are presented in Table 6. The results obtained give no ground for significant exceptions to the following statements: All of the rods developed maximum strength and shrinkage and minimum absorption when heated to 975° C. Heating to 1,000° C. was harmful. The minimum absorption was lower and the maturing range was shorter for bodies containing 5 per cent mullite than for bodies containing no mullite. Bodies made with a flux containing zinc (Nos. 60 and 61) showed a higher shrinkage and higher strength but not a lower absorption than the average for the series. The maturing range, whether or not it was desired to develop bodies of the lowest possible or of intermediate absorptions, did not exceed approximately 25° C.

The average values for modulus of rupture of the rods heated to 975° C. (Table 6) are very nearly equal to similar values which are found in the literature [11] for "semivitreous" bodies heated to cone 9 (about 1,250° C.) and which vary from 4,700 to 6,600 lbs./in.^{2}; but they are much lower than the values for vitreous bodies heated to cones 11 and 12 (about 1,285° and 1,310° C., respectively) which vary from 8,100 to 9,900 lbs./in.^{2}.

TABLE 6.—*Some properties of extruded bars (½ inch diameter by 6 inches long) heated for one-half hour at the temperatures indicated*

Body No.	900° C.			925° C.			950° C.			975° C.			1,000° C.		
	S	R	A	S	R	A	S	R	A	S	R	A	S	R	A
3B	1.4	3,000	8.0	2.1	3,400	6.5	2.2	3,500	5.0	3.0	4,000	3.5	3.1	3,500	2.0
4B	1.4	3,800	9.5	2.1	3,600	7.0	2.9	3,900	5.5	3.6	4,700	.5	3.1	4,000	4.5
7B	1.6	3,600	9.5	2.1	3,300	9.5	2.6	3,500	6.0	3.0	4,500	2.5	2.3	3,300	8.0
10B	1.7	3,200	10.0	3.1	3,700	7.5	3.8	4,500	5.0	4.9	4,300	3.5	3.3	3,500	7.0
11B	2.0	3,200	14.0	2.9	3,600	8.0	4.3	4,400	6.0	4.1	4,800	4.5	4.3	4,500	4.5
28B	1.4	3,300	12.5	2.5	3,800	9.0	3.3	4,400	7.0	3.5	4,600	6.0	3.5	4,300	5.0
3BM	1.6	3,600	9.0	2.0	4,100	6.0	2.2	3,900	5.0	3.6	4,600	.0	3.0	4,000	1.0
4BM	1.4	3,400	9.5	2.2	3,800	6.5	2.5	3,700	4.5	3.4	4,300	.5	2.5	3,400	4.0
7BM	1.6	3,800	8.0	2.0	3,800	6.0	2.5	4,000	3.5	2.8	4,600	.5	2.0	3,200	4.5
10BM	1.8	3,200	10.5	2.6	3,200	8.0	4.1	4,000	5.0	5.7	4,900	2.5	2.5	4,100	5.0
11BM	1.6	3,400	16.0	3.4	3,600	8.0	4.3	4,700	5.5	5.5	4,800	4.5	5.0	4,400	4.0
28BM	1.2	4,000	14.5	2.2	3,400	10.0	2.8	4,400	8.0	5.3	4,400	6.0	3.5	4,200	5.0

S=linear shrinkage, in per cent.
R=modulus of rupture, in pounds per square inch.
A=water absorption, percentage by weight.

(c) PROPERTIES OF DRY PRESSED TILE

(1) *Resistance to abrasion.*—The values obtained are given in Table 7. Apparently the compositions of the experimental bodies had no significant effect on their relative resistance to abrasion.

For comparison, three specimens of one brand of commercial white vitrified floor tile were tested and the average H_a value for nine determinations was 78. The following average H_a values are calculated from data in the report by Kessler:[12] Average of 45 marbles,

[11] E. E. Pressler and W. L. Shearer, B. S. Tech. Paper No. 310, 1926. R. F. Geller and A. S. Creamer, J. Am. Cer. Soc., vol. 14 (1), p. 30, January, 1931.
[12] See footnote 7, p. 477.

18; average of 15 limestones, 9; average of 14 slates, 8; average of 4 sandstones, 5.

(2) *Absorption.*—The absorption percentages reported in Table 7 are the lowest which it was possible to obtain without developing a vesicular or "overfired" structure. The group of bodies containing flux No. 3 has the lowest average absorption of the six groups differentiated by means of the flux. The BM series of bodies containing mullite but no kaolin has the lowest average absorption. Although there is little difference in the average absorption values given in Table 7 for the various series and groups, it should be remembered that those bodies containing flux No. 11 or No. 28 require a maturing temperature 30° C. higher than is required by the other bodies.

TABLE 7.—*Some properties of "dry pressed" tile*

Flux No.	Heat treatment		Resistance to abrasion;[1] series—				Absorption;[2] series—				Linear shrinkage;[3] series—			
	Maximum temperature, ±12° C.	Time at maximum temperature	B	BM	K	KM	B	BM	K	KM	B	BM	K	KM
	°C.	Hours	H_a value[4]				Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent	Per cent
3	960	2–3	44	45	42	43	2.0	1.0	2.5	1.5	4.5	4.0	5.0	4.5
4	960	2–3	42	41	40	44	3.5	2.5	3.5	3.0	4.5	4.0	4.0	3.5
7	960	2–3	41	40	41	39	1.0	1.5	3.0	3.0	3.0	2.5	3.5	3.0
10	960	2–3	45	45	40	40	3.5	2.5	4.5	4.5	4.5	4.0	4.0	4.0
11	990	3	52	39	45	49	2.5	2.0	4.0	3.0	6.0	5.0	5.5	5.5
28	990	3	51	53	42	44	3.0	1.5	5.0	3.0	4.5	5.0	4.5	4.5

	Standard deviation		Maximum individual deviation
	Maximum	Minimum	
H_a value	7	1	10
Absorption, per cent	1.3	.3	2.5
Shrinkage, do	.8	.2	1.7

[1] Bodies 3, 4, 7, and 10, values are average of 6 specimens from 2 heatings. Bodies 11 and 28, values are average of 3 specimens from 1 heating.

[2] Bodies 3, 4, 7, and 10, values are average of 9 specimens from 3 heatings. Bodies 11 and 28, values are average of 6 specimens from 2 heatings.

[3] Number of specimens used same as for absorption. These values are the total linear shrinkage during drying and heating.

[4] Calculated by means of the formula $H_a=\frac{10\,(2{,}000+W_s)\,G}{2{,}000\,W_s}$ (see footnote 7, p. 477) where:

W_s = weight of material lost by abrasion.
W_s = original weight of specimen.
G = apparent density.

The absorptions of 180 specimens representing 17 brands of commercial tableware were determined. The lowest average absorption for specimens of any one brand was 0.2 per cent, the highest 9.5 per cent, and the average for all brands was 7.2 per cent. The deviations for the experimental bodies (Table 7) may be compared with the following deviations for the commercial bodies: The maximum standard deviation, in per cent, for the specimens of a single brand was 2.1, the minimum 0.2; the maximum deviation of an individual specimen from the mean of a single brand was 5.0 per cent.

(3) *Linear shrinkage.*—The values for total percentage linear shrinkage during drying and heating are given in Table 7. The low values for the bodies containing flux No. 7 are an interesting development in view of the fact that these bodies are also among the least absorbent.

(4) *Color.*—None of the bodies are white. Within each series the colors vary according to the flux, as follows: Flux No. 28 produced the darkest body, then Nos. 7, 4, 3, 10, and 11. When compared with color standards [13] the B and BM series may be described as varying from cartridge buff, Plate XXX 19″ Y-O-Yf, toward white while the K and KM series vary from tilluel buff, Plate XL 17‴ O-Yf, toward white. Before making the comparisons the eyes of the investigator were tested for sensitivity to color in the colorimetry section, and found to be normal.

(5) *Resistance to crazing.*—The relative resistance to crazing is indicated by the values in Table 8. The BM series of bodies appears to have a resistance appreciably higher than the others and it will be noted that this series (Table 7) has the lowest average absorption. The total number of crazed specimens in the three groups containing flux Nos. 3, 7, or 28 is significantly lower than in the other three. No explanation for their apparently higher resistance was found.

(6) *Thermal expansion.*—The coefficient of thermal expansion of each of the bodies of the B and BM series was calculated from tests on one specimen of each body. (Table 9.) Their coefficients do not differ significantly from those of 16 commercial whiteware bodies (one test on each body) which varied from 6.7 to 7.5×10^{-6}.

TABLE 8.—*Relative translucency and resistance to crazing*

Flux No.	Tile [1]					Plates [2]					Relative translucency average applies to each series
	Maximum temperature ±10° C.	Number of specimens crazed (3 tested); series—				Maximum temperature ±10° C.	Number of specimens crazed (2 tested); series—				
		B	BM	K	KM		B	BM	K	KM	
3	960	1	0	0	0	945	0	0	1	0	"Bright".
4	960	2	0	2	0	950	1	0	2	2	Do.
7	960	0	0	1	1	940	0	0	0	0	Medium.
10	960	3	0	3	3	955	0	0	2	1	Between 28 and 11.
11	990	0	1	3	2	970	1	0	2	1	Nearly opaque.
28	990	0	0	1	0	980	0	0	1	1	Below medium.

[1] Bisque heated 3 hours at the maximum temperature. Glaze matured 1 hour at 950°±5°.
[2] Bisque heated from ½ to 1½ hours at the maximum temperature. Glaze matured at 950°±5°—time 1 to 1½ hours.

(d) PROPERTIES OF GLAZED PLATES

(1) *Resistance to crazing.*—Values indicating relative resistance to crazing are given in Table 7. The resistance of the BM series was highest and the average resistance of the "ball clay bodies" (B and BM) was higher than that of the "kaolin bodies" (K and KM), which is in agreement with the results of the tests on glazed tile. Results of the tests on tile and plates may not be directly comparable because the former were glazed on one side only while the latter were completely coated.

[13] Robert Ridgway, Color Standards and Color Nomenclature, printed by A. Hoen & Co., Baltimore, Md.

(2) *Translucency.*—The values for translucency, which are purely relative, were determined for three specimens of each body. As a means for comparison, plates of several brands of domestic vitrified hotel china (thickness 4.3 to 5.1 mm) were tested also. Their translucency varied from the arbitrarily selected "medium" to "bright." The light transmitted by the least translucent specimens (containing flux No. 11) was approximately of the same intensity as that transmitted by a specimen of commercial earthenware of 4 per cent water absorption.

The translucency values for the experimental bodies are given in Table 8 and, as indicated, they varied according to the flux. Other variations in body composition did not affect the light transmission sufficiently to be detected by the test method. That the bodies containing flux No. 11 are least translucent is explained probably by the fact that the flux itself is nearly opaque. (Table 1.)

TABLE 9.—*Coefficients of thermal expansion of bodies of the B and BM series*[1]

Body No.	Coefficient of expansion [2]	Body No.	Coefficient of expansion [2]
3B	7.6	3BM	7.4
4B	7.9	4BM	7.8
7B	8.6	7BM	9.1
10B	7.3	10BM	7.5
11B	6.5	11BM	6.4
28B	8.4	28BM	8.7

[1] The temperature range is from room temperature to a temperature below the point at which the body shows a marked increase in rate of expansion (approximately from 25° to 400° C.). The temperature at which the rate of expansion increases is nearly the same as the lower critical temperature of the flux used.
[2] Values to be multiplied by 10^{-6}.

V. SUMMARY

The results obtained in this investigation indicate that the production of ceramic bodies having water absorptions lower than the average for commercial earthenware, and maturing below 1,000° C., would require careful supervision and control of all of the manufacturing processes.

It would probably be necessary to wet-grind the flux with the other ingredients of the body to obtain a sufficiently fine-grained and uniform product. This would be done at the cost of introducing dissolved flux in the "slip."

No difficulty was encountered in forming tile and plates approximately 2 inches square and 3 inches in diameter, respectively, by the dry-press process in a laboratory press.

The particular body compositions used could not be matured on what would usually be considered a short heating schedule, since it was necessary to allow sufficient time for all organic matter to oxidize and volatile products to escape before the flux softened sufficiently to seal the pores of the body.

Comparatively small variations in the chemical composition of the flux or of the body in which it is used may have a disproportionate effect on the properties of the product. For example, the use of kaolin in place of 50 per cent of the ball clay decreased the resistance to abrasion of 9 out of 12 bodies (Table 7); the average absorption of

the bodies containing kaolin was about 50 per cent higher than the average for the others (Table 7) and their resistance to crazing when glazed was considerably lower (Table 8). Also, the substitution of kaolin for ball clay produced bodies slightly darker in color. The results, therefore, indicate that it would be advantageous to use all ball clay, preferably "washed" and low in organic matter, rather than a mixture of ball clay and kaolin.

The introduction of 5 per cent of "mullite" at the expense of the clay appeared to have some desirable effects. (Tables 7 and 8.)

Within any one series of bodies the flux appeared to be the predominating factor in determining the relative color and translucency of bodies. (Table 8.) Effects on the other properties are not so pronounced.

It is believed that at least some of the fluxes have possibilities as bonds for certain classes of manufactured abrasive wheels.

VI. CONCLUSIONS

In general, it may be stated that ceramic bodies comparable in transverse breaking strength to earthenware, nearly white in color and varying in water absorption from 1 to 5 per cent, have been made in the laboratory by the dry-press process, of commercially available materials, and by maturing below 1,000° C. The bodies may be expected to resist mechanical abrasion better than nonceramic flooring materials, such as marble, and glazed specimens resisted crazing satisfactorily in laboratory tests. There are no data available on which to base conclusions regarding the cost of manufacture under commercial conditions.

WASHINGTON, May 9, 1932.

RP484

THE DETERMINATION OF MAGNESIA IN PHOSPHATE ROCK

By James I. Hoffman

ABSTRACT

A method for the determination of magnesia in phosphate rock is presented. Calcium is separated as sulphate in alcoholic solution, and magnesium is determined in the filtrate by precipitating it as magnesium ammonium phosphate. Citric acid is added to prevent interference by iron, aluminum, and titanium. In this procedure part of the manganese always accompanies the magnesium. This is determined in the ignited residue by the periodate method. The data show that arsenic does not interfere and that the method is also applicable if larger amounts of magnesium are present than are usually found in phosphate rock.

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I. INTRODUCTION

Practically all samples of phosphate rock contain less than 0.5 per cent of magnesia. To determine this a procedure must be used in which large amounts of calcium and moderate amounts of iron, aluminum, titanium, manganese, and fluorine are eliminated. Calcium can be separated by precipitating it as oxalate in an oxalic acid solution,[1] or as sulphate in an alcoholic solution. If the former procedure is used, the precipitation with oxalate must be repeated. Precipitating calcium as sulphate is more suitable in this case because the separation of small amounts of magnesium is so nearly complete in a single precipitation that the operation need not be repeated. Iron, aluminum, titanium, and part of the manganese are eliminated if magnesium is precipitated as magnesium ammonium phosphate in a solution containing ammonium citrate, and a correction for any manganese which is precipitated can be applied to the finally weighed residue. Fluorine is eliminated at the start by evaporating with sulphuric acid. Arsenic, if it is not previously eliminated, is volatilized during the evaporation of the alcohol after the calcium sulphate is separated.

The following method was found to yield satisfactory results when applied to synthetic mixtures and to the Bureau of Standards

[1] G. E. F. Lundell and J. I. Hoffman, The Analysis of Phosphate Rock, J. Assoc. Official Agric. Chem. vol. 8, p. 184, 1924.

standard sample of phosphate rock, No. 56, which has the following percentage composition: P_2O_5, 31.3; Fe_2O_3, 3.3; Al_2O_3, 3.1; CaO, 44.8; SiO_2, 6.7; TiO_2, 0.15; MnO, 0.25; MgO, 0.32; F, 3.6. This composition is typical of phosphate rocks excepting that in most cases smaller percentages of the oxides of manganese and magnesium are present.

II. METHOD FOR THE DETERMINATION OF MAGNESIA

Transfer 2 g of phosphate rock, ground to pass a No. 100 sieve and dried for one hour at 105° C., to a 250 ml beaker, cover, add 15 ml of diluted hydrochloric acid (2+1)[2] and 5 ml of nitric acid, and boil gently for 10 to 15 minutes. Remove the beaker from the source of heat, add 6 ml of diluted sulphuric acid (1+1), remove the cover, and evaporate until fumes of sulphuric acid appear. Cool slightly, wash down the inside surface of the beaker with a jet of water and again evaporate until fumes of sulphuric acid appear. Cool, add 10 ml of water, stir thoroughly, and digest on the steam bath for 10 to 15 minutes. Remove from the steam bath, add 100 ml of 95 per cent alcohol,[3] stir so that the calcium sulphate is well dispersed throughout the liquid, and then allow to stand for 30 minutes or longer. Filter by means of suction through a tight plug of filter paper pulp, using a Gooch crucible, carbon funnel, or Büchner funnel, and wash five times with 5 ml portions of 95 per cent alcohol containing 1 ml of sulphuric acid per 100 ml.

Evaporate the alcoholic filtrate as far as possible on the steam bath. Transfer the solution to a 300 ml Erlenmeyer flask, dilute to 75 to 100 ml, and add 2 g of citric acid and 15 ml of a 25 per cent solution of diammonium phosphate, $(NH_4)_2HPO_4$. Add ammonium hydroxide until the solution is alkaline to litmus and then add 10 ml in excess. Add 5 to 10 glass beads, tightly stopper the flask, and shake on a shaking machine for at least one hour. Allow to stand in a cool place for four hours or preferably overnight. Filter through a tight paper containing a little paper pulp, and wash with diluted ammonium hydroxide (5+95), containing 50 g of diammonium phosphate per liter, until the precipitate and paper are free from iron and aluminum. Pass 25 ml of hot diluted hydrochloric acid (5+95) through the paper into the flask, transfer the solution to a 150 ml beaker, and wash the paper and flask thoroughly with more of the diluted acid. To the solution in a volume of 50 to 75 ml and containing no glass beads, add ½ ml of a 25 per cent solution of diammonium phosphate, cool, and then add ammonium hydroxide slowly and with stirring until the solution is alkaline to litmus. Stir for a few minutes, then add 3 to 4 ml of ammonium hydroxide and allow to stand for four hours or overnight. Transfer the precipitate to a small filter and wash with diluted ammonium hydroxide (5+95). Transfer the paper and precipitate to a platinum crucible, ignite slowly at a temperature below 900° C. until the carbon is burned (preferably in a muffle furnace with pyrometric control), and then at about 1,100° C. for one to two hours. Cool and weigh.

[2] This denotes 2 volumes of hydrochloric acid, specific gravity 1.18, mixed with 1 volume of water. This system of designating the diluted acids or ammonium hydroxide is used throughout this paper. If no dilution is specified, the concentrated reagent is intended.

[3] In most of this work 95 per cent ethyl alcohol was used. Mixtures of 100 parts of 95 per cent ethyl alcohol with from 5 to 25 parts of methyl alcohol proved equally satisfactory.

The residue consists of $Mg_2P_2O_7$ and possibly $Mn_2P_2O_7$ and $Ca_3(PO_4)_2$. If the alcoholic filtrate was clear, the tricalcium phosphate, $Ca_3(PO_4)_2$, will not exceed 0.3 mg and can be neglected unless very accurate results are desired.[4] The correction for manganese is made as follows: Dissolve the residue in 10 ml of diluted sulphuric acid (1+9), transfer the solution to a 300 ml Erlenmeyer flask, and add 50 ml of diluted nitric acid (1+3), 2 ml of sirupy phosphoric acid, specific gravity, 1.7, and 0.2 g of potassium periodate, KIO_4. Boil for 15 to 20 minutes, cool, and dilute to a convenient volume. In another flask containing the same amounts of the reagents treated in a similar way, match the color by adding a standard solution of potassium permanganate. From the volume of the solution of permanganate required, calculate the weight of $Mn_2P_2O_7$ in the residue Subtract this weight from the total weight, and regard the difference as $Mg_2P_2O_7$, which contains 36.21 per cent of MgO.

Table 1 gives results obtained by this method for magnesia in phosphate rock and in mixtures approximating the composition of phosphate rock. The standard value for magnesia (0.32 per cent) in the Bureau of Standards standard sample of phosphate rock, No. 56, was obtained by twice precipitating the calcium as oxalate in dilute oxalic acid solution [5] and determining the magnesia in the combined filtrates by precipitating as magnesium ammonium phosphate in the presence of ammonium citrate and then igniting to magnesium pyrophosphate. Corrections were made for calcium and manganese.

TABLE 1.—*Results obtained for magnesia in phosphate rock and in synthetic mixtures*

Analysis No.	Material analyzed	MgO present or added	MgO found	MgO present or added	MgO found	Error
1	0.12 g Fe_2O_3+0.12 g Al_2O_3+0.1 g CaF_2+1.65 g $Ca_3(PO_4)_2$	*g* 0.0008	*g* 0.0007	*Per cent* 0.04	*Per cent* 0.035	*Per cent* −0.005
2	do	.0008	.0008	.04	.04	.000
3	do	.0032	.0031	.16	.155	−.005
4	do	.0079	.0078	.395	.40	+.005
5	do	.1140	.1130	5.70	5.65	−.05
6	0.12 g Fe_2O_3+0.12 g Al_2O_3+0.1 g CaF_2+.0015 g MnO +1.65 g $Ca_3(PO_4)_2$	.0032	.0034	.16	.17	+.01
7	do	.0032	.0030	.16	.15	−.01
8	0.12 g Fe_2O_3+0.12 g Al_2O_3+0.1 g CaF_2+0.0045 g MnO +1.65 g $Ca_3(PO_4)_2$	.0079	.0079	.395	.395	.000
9	2.0 g Bureau of Standards standard sample of phosphate rock No. 56			.32	.32	.00
10	do			.32	.33	+.01
11	do			.32	.31	−.01
12	2.0 g Bureau of Standards standard sample of phosphate rock No. 56+0.0092 g MgO			.78	.79	+.01
13	2.0 g Bureau of Standards standard sample of phosphate rock No. 56+0.0175 g As_2O_3			.32	.31	−.01

[4] If a correction for calcium is to be made, dissolve the residue in 10 ml of diluted sulphuric acid (5+95), evaporate to about 5 ml, and then add 25 ml of 95 per cent alcohol. Allow to stand for one to two hours, filter on a small paper, and wash with alcohol. Dry the paper in the funnel and dissolve the precipitate of calcium sulphate in 20 ml of hot diluted hydrochloric acid (1+99). Add a few crystals of ammonium oxalate, heat, render the solution faintly ammoniacal, and allow to stand for one-half to one hour. Filter, ignite, and weigh as CaO. Calculate to tricalcium phosphate, $Ca_3(PO_4)_2$, and subtract from the apparent weight of $Mg_2P_2O_7$.

If calcium is determined in this way, the alcoholic filtrate is used for the determination of manganese. Before applying the periodate oxidation, this filtrate must be evaporated and heated until fumes of sulphuric acid appear, and then treated with nitric acid to make sure that reducing substances are absent.

[5] See The Analysis of Phosphate Rock, J. Assoc. Official Agric. Chem., vol. 8, p. 203; 1924.

The magnesium that was used in making up the mixtures was added in the form of a standard solution of magnesium chloride. The iron and aluminum were added as solutions of their chlorides. The Bureau of Standards standard sample of fluorspar No. 79 was used as the source of the CaF_2 added. The percentage composition of this sample is: CaF_2, 94.8; $CaCO_3$, 2.17; SiO_2, 1.9; Zn, 0.35; Pb, 0.23; S, 0.13; Fe_2O_3, 0.15; Al_2O_3, 0.02; MgO, 0.13. The tricalcium phosphate that was used contained 0.3 mg of MgO in 1.65 g. Proper corrections were made for the magnesia thus introduced.

The calcium sulphate obtained by precipitation with alcohol in analysis No. 5 was dissolved in hot hydrochloric acid and then evaporated with 6 ml of diluted sulphuric acid (1 + 1). The precipitation by alcohol was repeated and the magnesia determined in the filtrate as before. The amount of MgO found was 0.0011 g. This indicates that if large amounts of magnesium are present, some is retained by the calcium sulphate. Less than 0.005 per cent of MgO was retained by the calcium sulphate in the case of phosphate rock No. 56 (analyses Nos. 9 to 13).

III. DISCUSSION OF THE METHOD

1. DECOMPOSITION OF THE SAMPLE

A 2 g sample each of Tennessee brown rock (MgO − 0.02 per cent), Tennessee blue rock (MgO − 0.36 per cent), Florida pebble rock (MgO − 0.25 per cent), Florida hard rock (MgO − 0.05 per cent), Wyoming phosphate rock (MgO − 0.08 per cent) and Idaho phosphate rock (MgO − 0.31 per cent)[6] was decomposed by treatment with hydrochloric and nitric acids as described in the preceding section. The following test was made to determine the amount of magnesia in the insoluble residue: After adding 50 ml of water and digesting, the insoluble matter was collected on a filter, washed, and ignited in platinum. The ignited residue was brought into solution by treating with hydrofluoric and sulphuric acids and then evaporating until fumes of sulphuric acid were copiously evolved. The contents of the crucible were transferred to a small beaker by means of 25 to 30 ml of 95 per cent alcohol, and the calcium sulphate which separated was removed by filtration. Magnesium was determined in the filtrate by the method above outlined for the determination of magnesia in phosphate rock. An average of less than 0.005 per cent of magnesia, MgO, was found in the insoluble matter, and in no case did the percentage exceed 0.01.

2. SEPARATION OF CALCIUM SULPHATE BY MEANS OF ALCOHOL

The results in the table show that the separation of calcium sulphate by means of alcohol is very satisfactory for the small amounts of magnesium present in phosphate rock and that it is applicable even if much larger amounts are involved. The amount of sulphuric acid specified is the minimum that should be used, because if the sulphates become dry and form a cake during the evaporation with sulphuric acid, it is difficult to extract all of the magnesium with

[6] These representative samples were furnished through the courtesy of K. D. Jacob, of the United States Department of Agriculture.

alcohol. There is less danger of calcium sulphate running through the filter if a little sulphuric acid is added to the alcohol used for washing and if the filter is not allowed to run dry. The presence of considerable amounts of organic matter, such as are found in some samples of phosphate rock, does not adversely affect the separation.

3. PRECIPITATING MAGNESIUM AS MAGNESIUM AMMONIUM PHOSPHATE

In order to avoid tedious separations, it is desirable to precipitate the magnesium in the presence of the iron and aluminum. About 2 g of citric acid must be added to hold in solution the amounts of these elements that may be expected in phosphate rock. In such solutions it is difficult to precipitate small amounts of magnesium ammonium phosphate. In some cases complete precipitation is not obtained even if the solution is vigorously stirred or shaken mechanically, but if the solution is shaken in a flask containing a few glass beads, complete precipitation can readily be had. The precipitate thus obtained is very finely divided, which necessitates the use of a very tight filter. The most satisfactory filtering medium consists of a tight paper containing some fine paper pulp. Glass beads are not used in the second precipitation.

If small amounts of magnesium, such as are likely to be encountered in phosphate rock, are precipitated as magnesium ammonium phosphate in the presence of ammonium citrate without agitation, a few hours are sometimes required before the crystals begin to separate. These transparent crystals adhere to the beaker and stirring rod and are slightly soluble in the ordinary wash solutions. If they are broken in transferring them to the paper, more will dissolve in the wash water than if they remain undisturbed.

If manganese is present in a solution in which magnesium ammonium phosphate is precipitated, it is quantitatively precipitated under the usual conditions such as are outlined for the last precipitation, but if citric acid is added, as in the first precipitation, less than one-third of the manganese accompanies the magnesium when the two are present in the proportions usually found in phosphate rock. This quantity is not constant, and it is necessary to determine the manganese in the ignited residue that is finally obtained. If it is known that the phosphate rock contains less than 0.02 per cent of manganese oxide (MnO), the correction may be neglected.

IV. ACKNOWLEDGMENT

Acknowledgment is made to Dr. G. E. F. Lundell for technical advice.

WASHINGTON, July 6, 1932.

RP485

COLLISIONS OF THE FIRST AND SECOND KIND IN THE POSITIVE COLUMN OF A CÆSIUM DISCHARGE

By F. L. Mohler

ABSTRACT

The power input minus the power lost by recombination at the tube walls measures the number of quanta dissipated by inelastic collisions at the resonance potential, 1.42 volts. For low-pressure low-current conditions this is equal to the number of collisions $C_{1\,2}$ and the effective area for a collision is

$$q_{1\,2}=5.4\pm.6\times10^{-15}\ \text{cm}^2$$

At higher pressures and currents collisions of the second kind give energy back to the electrons and the number of quanta dissipated is $C_{1\,2}-C_{2\,1}$ where $C_{2\,1}$ is the number of collisions of the second kind. This gives a basis for computing the number of excited atoms n_2. The value of n_2 can also be measured spectroscopically by analysing light from an incandescent lamp passed through the discharge and finding the lamp temperature T_L at which absorption lines match the background. T_L is nearly the electron temperature, confirming the evidence that collisions of the first and second kind become nearly equal in number.

The measured radiation intensity is equated to the radiation at a temperature T_L over a spectrum range $\Delta\lambda$ to find $\Delta\lambda$. This effective width of the resonance lines ranges from 0.6 to 19 A between 0.006 and 0.35 mm pressure. At constant pressure the radiation is proportional to n_2 and the ratio gives the depth of the layer of vapor from which the radiation comes; 0.003 to 0.001 mm in the above pressure range.

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I. INTRODUCTION

In a recent paper I have reported measurements of power input and power losses in the positive column of a cæsium discharge.[1] The experimental material included radiation measurements and measurements of probe characteristics for a wide range of currents and pressures in tubes 1.8 cm in diameter. The present paper uses these measurements as a basis for a study of the atomic processes involved in the dissipation of power. It was found that in general

[1] F. L. Mohler, Power Input and Dissipation in the Positive Column of a Cæsium Discharge, B. S. Jour. Research, vol. 9 (RP455), p. 25, July, 1932. Referred to as RP455 in the text.

the radiation is an important part of the power loss and that most of the radiation is in the first doublet of the principal series at 8,521 and 8,944 A. The excitation potential is 1.42 volts, and it is known from critical potential experiments[2] that this excitation gives the predominant type of inelastic collision in cæsium. This justifies the approximation that the power input is expended in inelastic collisions at the first resonance potential and in ionization, and that other excitation processes are negligible. This view of the power loss has been proposed and critically examined for the case of the mercury positive column by Killian.[3]

I will assume that the power lost by inelastic collisions at the first resonance potential is equal to the power input minus the power lost by recombination of ions at the walls; $P-W$ per centimeter of the column in the notation of RP455. For low pressure low current conditions this is practically equal to the radiation loss and is entirely justified; but, at the other extreme, my assumption becomes rather arbitrary. If ionization by collision with excited atoms is important, then part of the loss W is at the expense of inelastic collisions. If recombination in free space is important, then W does not account for the full ionization loss. The energy per collision or per quantum is $eV_r = 2.26 \times 10^{-19}$ joules, where V_r is the excitation potential; and the number of quanta dissipated is $(P-W)/2.26 \times 10^{-19}$ per centimeter of the column per second.

The number of inelastic collisions per centimeter of the column per second, $C_{1\,2}$, can be expressed in terms of the effective collision area $q_{1\,2}$ of an atom for such a collision.

$$C_{1\,2} = q_{1\,2} N_e n_1 v_e f(v)$$

where N_e is the number of electrons per cm of the column, n_1 is the number of atoms per cubic centimeter (accurately the number in the normal state), v_e is the electron velocity and $f(v)$ is the fraction of electron-collisions with kinetic energy greater than eV_r. The electrons have a Maxwell distribution of energy, here expressed in terms of V_0, where

$$eV_0 = kT = 2/3 \text{ mean energy}$$

Introducing for $f(v)$ the integral over energies between $V_r e$ and infinity

$$C_{1\,2} = q_{1\,2} N_e n_1 v_e \left(\frac{V_R}{V_0} + 1\right) \exp\left(-\frac{V_R}{V_0}\right) \qquad (1)$$

The probability of an inelastic collision is a function of V which rises abruptly from zero at V_R to a maximum very close to V_R and then decreases less abruptly over a range of several volts.[4] $q_{1\,2}$ is the integrated effect of all electrons of a Maxwell distribution which exceed V_R and so it is a function of V_0 which presumably increases with decreasing V_0.

From the above remarks it seems to follow that the number of collisions is equal to the number of quanta dissipated.

$$C_{1\,2} = (P-W)/2.26 \times 10^{-19} \qquad (2)$$

[2] Foote, Rognley, and Mohler, Phys. Rev., vol. 13, p. 59, 1919.
[3] Killian, Phys. Rev., vol. 35, p. 1238, 1930.
[4] Darrow, Electrical Phenomena in Gases, Williams, Wilkins Co., 1932.

It will be shown that this identity is not justified except for low pressures and currents. Electron energy expended in producing excited atoms may be given back to the electrons by collisions of the second kind so that in general the power dissipated is less than $C_{1\,2}\times 2.26\times 10^{-19}$ watts. In general,

$$C_{1\,2}-C_{2\,1}=(P-W)/2.26\times 10^{-19} \tag{3}$$

where $C_{2\,1}$ is the number of collisions of the second kind per centimeter of the column per second.

II. EXPERIMENTAL PROCEDURE

The type of discharge tube was illustrated in RP455 (fig. 1). It was a termionic discharge in a tube 1.8 cm in diameter. Commonly there were two small probes near the axis and 12 cm apart to measure the voltage gradient, electron energy and electron concentration; and a disk electrode against the wall to measure the flow of ions to the wall. The cæsium was in a side tube, maintained at a lower temperature than the body of the tube. Vapor pressures were computed from the temperature by the relation [5]

$$\log p\ (mm)=-\frac{3{,}966}{T}+7.1650$$

The temperature measured by a thermocouple in contact with the tube wall in the region of the positive column was taken as the gas temperature in computing the number of atoms, n_1.

The discharge is characterized by exceptionally low electron speeds and high electron concentration. This makes the precision low, and an added difficulty is the electrical leakage over the cæsiated glass surfaces. The high electron concentration necessitates the use of a small probe surface. The leakage was greatly reduced by avoiding a close fit between the insulator and the probe but this leaves the effective collecting area uncertain. Two sizes of probe were used to cover the range of electron currents obtained; platinum wires 2 mm long and 0.4 mm in diameter, and wires of this diameter cut off flush with the insulator.

Figure 1 (taken from RP455) shows curves of the log of the probe current versus voltage relative to the anode for the two small probes 12 cm apart. The experimental points negative to the space potential (the intersection of the two lines) fall on a straight line showing that the electrons have a Maxwell distribution. The electron energy V_0 is given by the relation

$$V_0=(V_2-V_1)\log e/(\log I_1-\log I_2)$$

The experimental uncertainty is about 0.02 volt and, as V_0 may have values as low as 0.2 volt, the percentage error is high. Recognized sources of error tend to make V_0 too high. The value of V_0 at the tube wall is nearly the same as at the axis.

The random current density at the center of the tube, i_0, is given by the current at the space potential divided by the collecting area.

[5] Rowe, Phil. Mag., vol. 3, p. 534, 1927.

For the 2 mm probes the measured area 0.0257 cm² was used and the effective area of the wire, cut off flush with the insulator, was obtained by comparison with the 2 mm probe. This area 0.002 cm² is greater than the end of the wire because the edge is not completely insulated

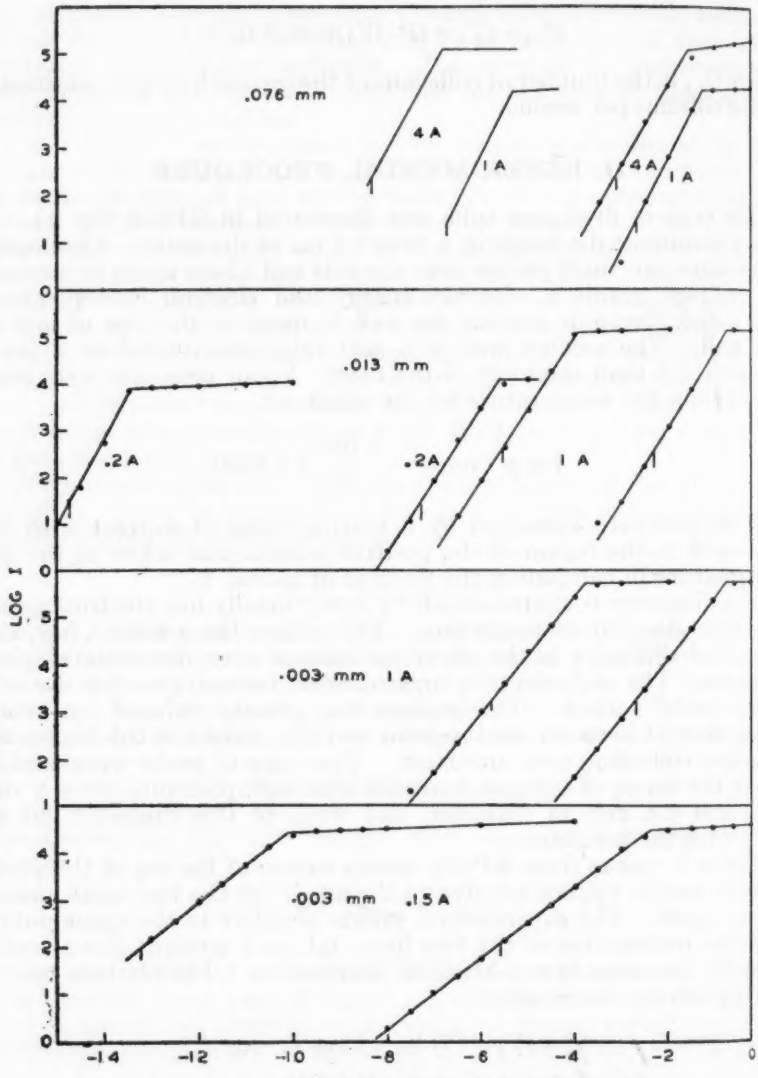

FIGURE 1.—*Probe characteristics for two small probes 12 cm apart at the axis of the positive column*

from the discharge. The number of electrons per cubic centimeter is given by the relation

$$n_0 = 2.51 \times 10^{19} i_0 / v_e$$

The space current decreases from the tube axis to the walls and the variation of current density across the diameter of the tube is roughly parabolic.[6] Two rather inaccurate experiments give a basis for estimating the total number of electrons per unit length of the tube from n_0. Comparison of the currents to a probe at the axis and a fine wire extending the full length of a radius gave the mean current density along the radius as 0.815 i_0. Assuming a parabolic distribution, the mean current density over the cross section is 0.72 i_0. In the second experiment the currents to similar probes at the axis and the walls were compared, and the value 0.325 i_0 for current density at the wall leads to a mean current density across the tube of 0.66 i_0 on the basis of a parabolic distribution. These experiments showed no systematic variation of distribution over a considerable range of pressure and current. The theoretical distribution for the case of low pressure and ionization proportional to the electron concentration gives a mean current density of 0.7 i_0.[7] I will use this value as it is consistent with the experimental values though the conditions do not conform to the postulates of the theory. Since v_e is constant

$$N_e = 0.7\pi r^2 n_0$$

Where r is the tube radius.

III. COLLISIONS OF THE FIRST AND SECOND KIND

Assuming that the number of inelastic collisions is equal to the number of quanta dissipated, neglecting collisions of the second kind, equations 1 and 2 give

$$q_{1\,2} = (P-W)/\left[2.26\times10^{-19}N_e n_1 v_e\left(\frac{1.42}{V_0}+1\right)\exp\left(-\frac{1.42}{V_0}\right)\right] \qquad (4)$$

Values of $q_{1\,2}$, computed on this basis from measurements at low pressures, are plotted in Figure 2 as a function of the discharge current. For pressures 0.003 and 0.0016 mm, there is a range of current, 0.5 amp and less, in which the value does not seem to depend on the current. There were 12 measurements in this range (some points in fig. 2 represent means of several measurements) which give a mean value

$$q_{1\,2} = 5.4 \pm .6\times10^{-15}\text{cm}^2$$

Any dependence of $q_{1\,2}$ on V_0 was concealed by the large experimental error; but, in view of the comparatively small range of values of V_0, this value can be used to give at least a rough estimate of the number of inelastic collisions under all conditions.

Brode's [8] measurements of the scattering of electrons by cæsium atoms give a value for the effective scattering area for 1.42-volt electrons of $56\times10^{-15}\text{cm}^2$. There are no direct measurements of $q_{1\,2}$. Loveridge [9] has obtained values for sodium and potassium based on absolute measurements of the radiation excited by a beam of electrons of uniform speed. His maximum value is about 1 per cent of

[6] Killian, Phys. Rev., vol. 35, p. 1238, 1930.
[7] Tonks and Langmuir, Phys. Rev., vol. 34, p. 876, 1929.
[8] R. Brode, Phys. Rev., vol. 34 p. 673, 1929.
[9] Loveridge, Univ. of Cal., Thesis, 1931.

the scattering area found by Brode. The experiment is extremely difficult and the uncertainty even greater than for the method used here. My value for cæsium is 10 per cent of the scattering area and this is an average value and not a maximum.

An examination of equation (4) shows the correlation between the curves of Figure 2 and other variables. At constant pressure the important variables are N_e and the exponential factor involving V_0. A curve of V_0 as a function of current is included in Figure 4. N_e increases roughly as the square of the current and up to 0.5 amp at 0.003 mm the decrease in V_0 compensates for the increase in N_e to keep the value of $q_{1\,2}$ constant. With higher currents, V_0 is constant and the increase in N_e gives a decrease in $q_{1\,2}$ that is entirely incompatible with the assumption that it measures a collision area. This is the case at all currents for higher pressures.

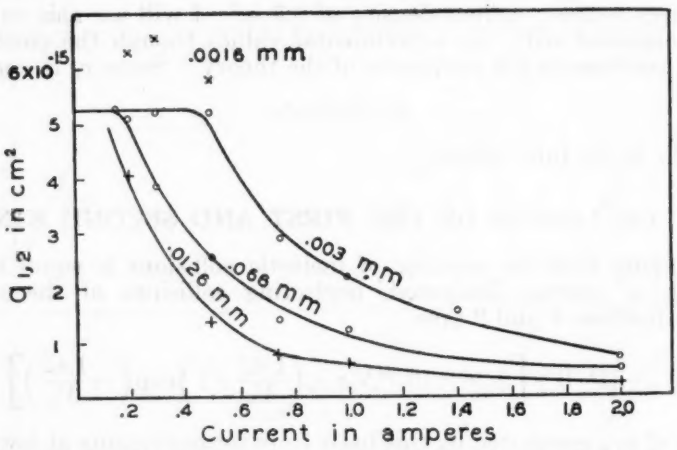

FIGURE 2.—*Values of $q_{1\,2}$ computed by equation (1) assuming that $C_{1\,2}$ is the number of quanta dissipated*

The difficulty is removed by the recognition that collisions of the second kind become increasingly important at higher currents. Figure 3 shows the data at 0.003 mm presented in accord with this idea. $C_{1\,2}$ is the number of collisions of the first kind as given by equation 1, and $C_{1\,2}-C_{2\,1}$ gives the number of quanta dissipated as given by equation 3. The two curves are nearly coincident up to 0.5 amp and above this point rapidly diverge with $C_{1\,2}$ nearly proportional to N_e. At high pressure it increases somewhat faster than N_e over the entire range of current. The number of collisions of the second kind, $C_{2\,1}$, is given by the difference between the two curves and it rises from a negligible quantity at 0.5 amp to 0.6 $C_{1\,2}$ at 1 amp, 0.8 $C_{1\,2}$ at 2 amps and 0.9 $C_{1\,2}$ at 3 amps. The predominant process at high currents is a reversible interchange of energy between the atoms and the electrons without dissipation of power.

The number of collisions of the second kind is expressed by an equation analogous to equation 1

$$C_{2\,1}=q_{2\,1}N_e n_2 v_e \tag{5}$$

where $q_{2\,1}$ is the effective area of the excited atoms and n_2 is the number of atoms per cubic centimeter in the excited state. $q_{2\,1}$ can be computed from $q_{1\,2}$ by the principle of detailed balance which states that in thermal equilibrium between cæsium atoms and electrons $C_{2\,1}$ must equal $C_{1\,2}$. Equations (1) and (5) are applicable to the equilibrium state at a temperature $T = V_0/11{,}600$. In equilibrium n_2 is given by Boltzmann's equation

$$n_2 = \frac{g_2}{g_1} n_1 \exp(-V_R/V_0) = 3n_1 \exp(-1.42/V_0) \tag{6}$$

where g_2 and g_1 are the weights of the $2P_{1\,2}$ and $1S_1$ states, respectively. Equating (1) and (5) and eliminating n_2 by equation (6) gives

$$q_{2\,1} = \frac{g_1}{g_2} q_{1\,2} \left(\frac{V_R}{V_0} + 1\right) \tag{7}$$

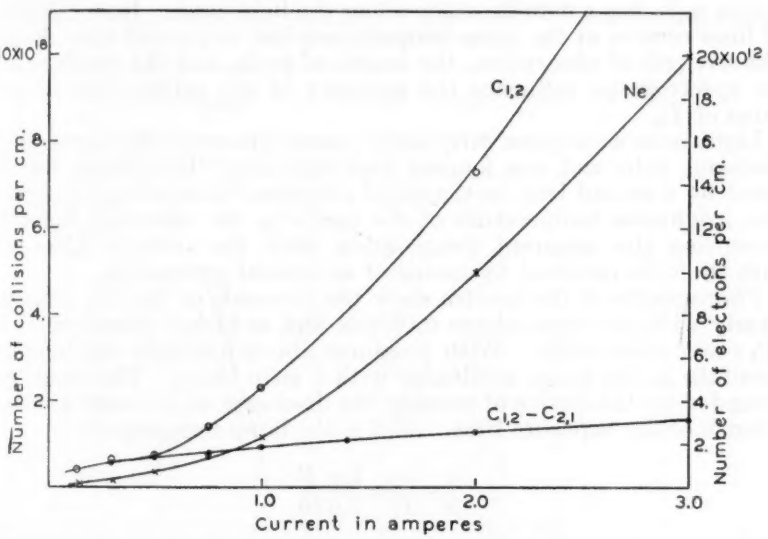

FIGURE 3.—*The number of collisions of the first kind and the number dissipated per cm of the column (left scale); the number of electrons per cm (right scale); from measurements at 0.003 mm pressure*

This is not the usual form of the Klein and Rosseland relation.[10] It is the equation applicable to all electrons of the Maxwell distribution and not to the particular speeds corresponding to V_0 and $V_R + V_0$.

Equation (5) now becomes

$$C_{2\,1} = \frac{1}{3} q_{1\,2} \left(\frac{V_R}{V_0} + 1\right) N_e n_2 v_e \tag{8}$$

This equation and equation (1) can be used to evaluate n_2 from the measured value of $C_{1\,2} - C_{2\,1}$. I will first give some direct experimental evidence as to the concentration of excited atoms.

[10] Klein and Rosseland, Zeits. für Phys., vol. 4, p. 46, 1921.

IV. THE NUMBER OF EXCITED ATOMS

A direct measure of the number of excited atoms can be obtained by a spectroscopic method which has been applied to measure flame temperatures. Light from an incandescent lamp is passed through the discharge and analyzed by a spectrograph. The resulting spectrum will show the cæsium absorption lines either as dark or bright lines, depending on whether the lamp temperature is above or below a critical temperature T_L, here called the reversal temperature. Hedwig Kohn [11] has shown that T_L, for a line emitted in a transition between states 2 and 1, differing in energy by $E_{2\,1}$, is related to the relative number of atoms in the two states by an equation identical in form to Boltzmann's equation

$$n_2/n_1 = (g_2/g_1) \exp(-E_{2\,1}/kT_L) \tag{9}$$

where the g's are the weights of the two states. The only assumption is that n_2/n_1 has a definite value along the light path. In equilibrium all lines reverse at the same temperature, but in general they do not. The strength of absorption, the length of path, and the resolution of the spectrograph influence the accuracy of the setting but not the value of T_L.

Light from a tungsten strip lamp passed diametrically through the discharge tube and was focused near the axis. The image was focused by a second lens on the slit of a 3-prism Steinheil spectrograph. The brightness temperature of the image in the tube was found by measuring the apparent temperature with the tube in place and with the tube removed by means of an optical pyrometer.

Photographs of the spectra show the reversals of the $2P_{1\,2}$ doublet clearly with pressures above 0.01 mm and at higher pressures T_L for $3P_{1\,2}$ was measurable. With pressures above 0.08 mm the temperature falls in the range attainable with a strip lamp. The range was extended by the device of keeping the discharge on for only a fifth or a tenth of the exposure time. If S is the lamp temperature

$$\frac{1}{S} - \frac{1}{T_L} = \frac{\log R}{7{,}320}$$

where R is the ratio of total exposure to the time the discharge is on. The method was checked in the range where T_L could be obtained by the lamp, but theoretically it is open to objection. The discharge lowers the vapor density so that n_1 is not the same as with the discharge off.

At the higher pressures the line at 8,521 A showed a sharp self-reversal which did not disappear at T_L. The resolution of 8,944 was less and it disappeared over a range of temperature of 50° or 100°. The failure of the method with high resolution and the range of uncertainty with low resolution comes from the variation of n_2/n_1 across a diameter.

In Table 1 and Figure 4 reversal temperatures are expressed in terms of electron volts ($V_L = T_L/11{,}600$) for comparison with values of V_0 measured electrically. The experimental error in V_0 is considerably larger than the inherent uncertainty in V_L. In equilibrium $V_L = V_0$

[11] Kohn, Phys. Zeits., vol. 29, p. 49, 1928.

and under actual discharge conditions V_L must be somewhat less than V_0 and the difference should decrease with increasing current and pressure. The observed differences are in the right direction, but the variation with current and pressure is not systematic. All differences fall within the range of the estimated error in V_0 so there is little basis for computing the departure from equilibrium. Reversals could not be measured at the lowest pressures where a large difference is to be expected. The small difference between values of T_L for 2P and 3P is real and shows that the number of atoms in the 3P state is further from the equilibrium value than the 2P state.

The results confirm the prediction that at moderate pressures and currents there is nearly an equilibrium between the electrons and the atoms in the first excited state. Or accepting this view they give a desirable check on the electrical method of measuring electron temperatures. Values from curves of Figure 4 (the upper one where there are two) will be taken for V_0 in the following computations.

TABLE 1.—*Electron temperature and reversal temperature in electron volts and the number of excited atoms*

Pressure	Current	V_0	V_L (2P)	V_L (3P)	$\frac{n_2}{n'_2}$ (2P)	$\frac{n_3}{n'_3}$ (3P)
mm	*Amp.*	*Volts*				
0.35	0.5	0.185	0.168	0.161	0.73	0.27
	1	.200	.180	.174	.91	.50
	2	.217	.195	.186	.96	.45
.16	.2	.175	.179	.163	----	----
	.5	.183	.184	.171	.79	.22
	1.0	.205	.192	.180	.93	.33
	2	.220	.206	.192	.97	.37
.076	.2	.200	.189	.174	----	----
	.5	.205	.195	.180	.81	.20
	1.0	.218	.202	.186	.93	.27
	2	.228	.211	.199	.97	.45
.032	.5	.232	.216	----	.76	----
	1	.232	.218	----	.92	----
	2	.238	.224	----	.96	----
	4	.266	.236	----	.97	----
.0126	.2	.257	.228	----	----	----
	.5	.257	.246	----	.61	----
	1	.257	.249	----	.87	----
	2	.257	.251	----	.95	----
	4	.291	.263	----	.96	----
.0056	.2	.298	.270	----	----	----
	.5	.283	.276	----	----	----
	1.0	.283	.288	----	.72	----
	2	.283	.283	----	.91	----

The actual values for the number of excited atoms can best be computed from the value of $C_{1\,2}-C_{2\,1}$ with $C_{1\,2}$ and $C_{2\,1}$ as given by equations 1 and 8.

$$C_{1\,2}-C_{2\,1}=q_{1\,2}N_e v_e\left(\frac{V_R}{V_0}+1\right)\left[n_1\exp\left(-\frac{V_R}{V_0}\right)-\frac{1}{3}n_2\right]$$

$$n_2=n'_2-3(C_{1\,2}-C_{2\,1})/\left[q_{1\,2}N_e v_e\left(\frac{V_R}{V_0}+1\right)\right] \qquad (10)$$

where

$$n'_2=3n_1\exp\left(-\frac{V_R}{V_0}\right)$$

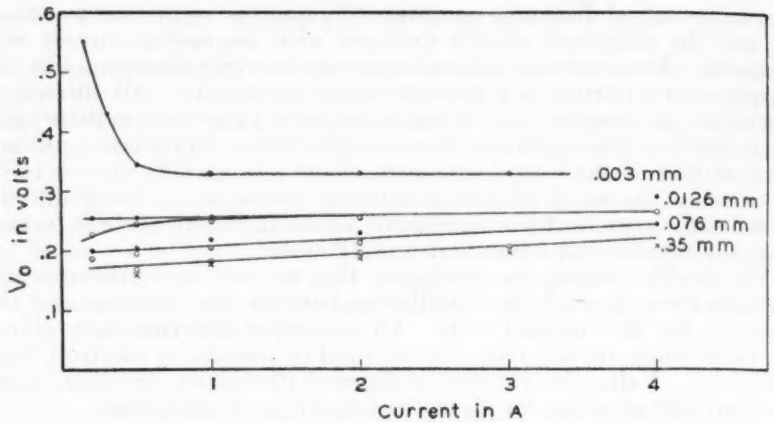

FIGURE 4.—*Measurements of electron energy V_0 shown by dots, V_L from reversal temperature of $1S-2P_{12}$ shown by circles, V_L from reversal temperature of $1S-3\ P_{12}$ shown by crosses*

Equation 10 gives the number of excited atoms in terms of the number that would exist in equilibrium at the electron temperature minus a term that becomes very small for high pressures and currents. Thus the fact that experimental uncertainties in the term on the

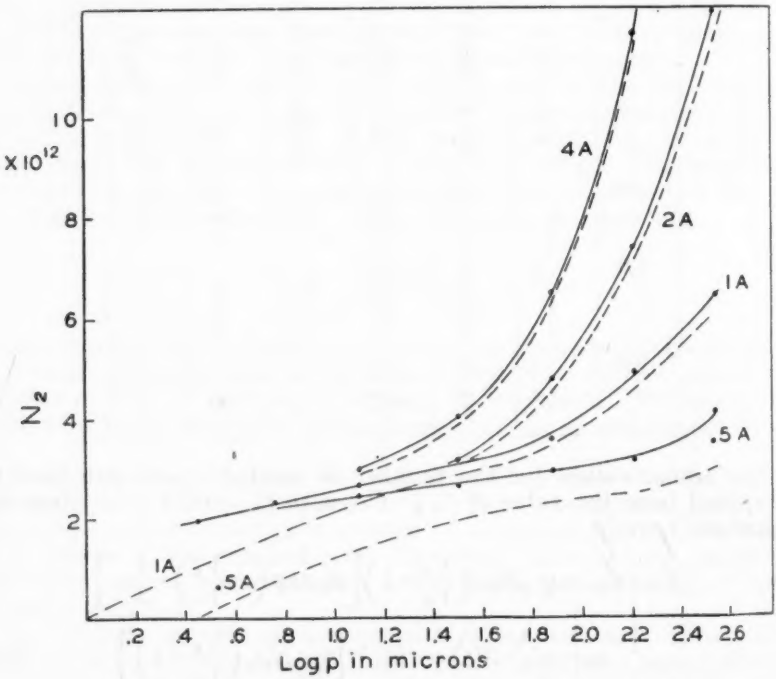

FIGURE 5.—*The number of excited atoms in the $2P_{12}$ states*

Full lines are the number that would exist in equilibrium at the electron temperature; broken lines give the actual number as estimated by equation 10.

right may become large under these conditions does not seriously affect the conclusions.

In Figure 5 the solid lines are values of n'_2 computed from V_0 as given in Figure 4. The broken lines are values of n_2 as given by equation 10. The values of n'_2 increase slowly with pressure, the equilibrium concentration n'_2/n_1 decreases. For 0.5 amp it ranges from 3.4×10^{-2} at 0.003 mm to 7×10^{-4} at 0.35 mm. Table 1 includes values of the ratio n_2/n'_2 which is a measure of the approach to equilibrium and Figure 6 shows this ratio as a function of the current. Dots are computed by equation 10 and are fairly accu-

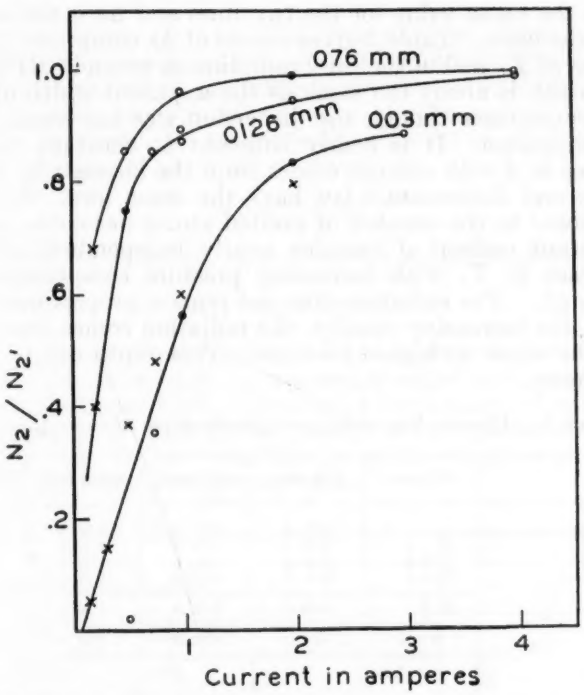

FIGURE 6.—*The ratio of the number of excited atoms to the equilibrium number measuring the approach to equilibrium as a function of current*

Dots are based on equation 10 while crosses are computed from the assumption that n_2 is proportional to the radiation intensity.

rate as the ratio approaches 1. The values become indeterminate at low current because of arbitrary assumptions in the derivation of 10. It will be shown in the following section that n_2 is roughly proportional to the intensity of the radiation, and the crosses in Figure 6 have been computed on this basis from a single high-current value of n_2 as given by equation 10. The rapid decrease in the ratio at low current comes in large part from the increase in n'_2 Table 1 includes some values of the ratio n_3/n'_3 for the $3P_{1\,2}$ state. This is derived from the tabulated values of n_2/n'_2 and the difference in T_L for the two doublets.

V. RADIATION INTENSITY AND REVERSAL TEMPERATURE

The luminous cæsium vapor is transparent except at the absorption lines and over the width of the lines it is completely opaque. The cæsium radiation may be considered as the radiation of an incandescent body at the temperature T_L which has zero emissivity except at the resonance lines. (The contribution of other lines is negligible.) The radiation per cm² can be expressed in the form of Wien's law:

$$J = C_1 \lambda^{-5} \exp\ (-V_R/V_L)\ \Delta\lambda$$

where λ is the mean value for the two lines and $\Delta\lambda$ is the sum of the widths of the lines. Table 2 gives values of $\Delta\lambda$ computed from measured values of T_L and of the total radiation as given in RP455. This effective width is about the same as the apparent width of the lines on the spectrograms though the dispersion was too small for an accurate comparison. It is nearly constant at constant pressure, so the increase in J with current comes from the increase in T_L. Since Wien's law and Boltzmann's law have the same form, the radiation is proportional to the number of excited atoms per cubic centimeter.

At constant current J remains nearly independent of pressure. The decrease in T_L with increasing pressure compensates for the increase in $\Delta\lambda$. The radiation does not remain proportional to n_2 for, because of the increasing opacity, the radiation comes from a smaller depth of the vapor at higher pressure. This depth can be estimated as given below.

TABLE 2.—*Effective line width and effective depth of radiating vapor*

	0.35 mm	0.16 mm	0.076 mm	0.0126 mm	0.0056 mm
0.2 ampere		8.5 A	5.6 A	1.25 A	0.55 A
0.5 ampere	20 A	9.35 A	5.64 A	1.48 A	.603 A
1.0 ampere	18.6 A	9.45 A	5.5 A	1.37 A	.625 A
2.0 amperes	17.8 A	9.0 A	5.86 A	1.52 A	.725 A
$\Delta\lambda$ mean	18.8	9.05 A	5.65 A	1.40 A	.626
Δr in cm	1.22×10^{-3}	1.42×10^{-3}	1.62×10^{-3}	2.28×10^{-3}	3.1×10^{-3}
$\frac{\Delta\lambda\times10^{-13}}{\Delta r\times n_1}$	2.6	2.3	2.5	2.8	1.9

The rate of radiation of atoms in the $2P_{1\ 2}$ states is very closely that of a classical oscillator of the frequency of the cæsium lines[12]

$$A = \frac{8\pi^2 e^2}{3\ c\ m\lambda^2} = 2.8\times10^7 \text{ per second}$$

The radiation from n_2 atoms is then $2.8\times10^7\ n_2$ quanta per second. The measured radiation per square centimeter, divided by this number, gives the volume or the depth from which the radiation comes. Values of this effective depth, Δr, are included in Table 2 and range from 1 to 3×10^{-3} cm. The ratio $\Delta\lambda/\Delta r$ should be proportional to the number of atoms per cubic centimeter. The last row of the table shows that this proportionality holds except perhaps for the lowest pressure.

[12] Handbuch der Phys., vol. 20.

VI. DURATION OF EXCITED STATES

While the radiation life of an excited atom is $1/A = 3.56 \times 10^{-8}$ seconds, the duration of excitation within the discharge tube may be much longer than this. The radiation will be absorbed and reemitted in a distance comparable with Δr computed in the preceding section. If this experimental quantity is taken as the mean free path of a quantum of resonance radiation, then the time of diffusion of resonance radiation out of the cylindrical tube will be—

$$\tau_r = 0.75\ (r/\Delta r)^2 \times 3.56 \times 10^{-8} = 0.015 \text{ to } 0.0025 \text{ second} \qquad (11)$$

using extreme values of Δr. This can only be right in order of magnitude because of the approximations used in the derivation of Δr.

The actual duration of the excited state in the discharge, τ, will be shorter than this because of collisions of the second kind. This time can be computed by equating the number of excited atoms to the rate of production times the duration—

$$n_2 = C_{12}\ \tau/\text{vol} \qquad (12)$$

The time between collisions τ_{21} is given by the relation—

$$1/\tau_{21} = q_{21}\ N_e v_e/\text{vol} \qquad (13)$$

Some values are given in Table 3 and it is seen that except at low currents and pressures τ and τ_{21} are nearly equal and by equation 13 inversely proportional to N_e which has a large range of values. The extreme value of $\tau = 3.8 \times 10^{-8}$ is nearly equal to the radiation life which means that in the 4 amp discharge the duration of an excited state is reduced to half its normal value.

TABLE 3.—*The duration of excited states and the time between collisions*

Pressure	Current	τ	τ_{21}	τ_0
mm	*Amperes*			
0.003	2	0.58×10^{-6}	0.70×10^{-6}	3.3×10^{-6}
	1	1.54	2.65	3.7
	.5	3.24	12	4.4
	.15	4.95	90*	5.2
.0126	2	.25	.264	5.0
	1	.77	.88	5.9
	.5	1.90	3.0	5.9
.076	4	.038		
	2	.098	.101	3.3
	1	.28	.30	4.0
.35	2	.094	.098	2.5
	1	.24	.26	2.9

The duration of an excited state in the absence of collisions of the second kind τ_0 is given by—

$$\frac{1}{\tau_0} = \frac{1}{\tau} - \frac{1}{\tau_{21}} \qquad (14)$$

It can be shown that $\tau_{21}/\tau = n'_2/n_2$ so that the small quantity $1/\tau_0$ can be evaluated by equation (14) in spite of experimental errors in τ

and τ_{21}. The values τ_0 which remain of the magnitude 5×10^{-4} seconds for all conditions are much smaller than the diffusion times as given by equation 11. Possibly collisions of the first kind with excited atoms are a more important factor than diffusion. However, the diffusion time and τ_0 are quantities of secondary importance in the discharge and, as the theory has been limited to first-order approximations, conclusions as to second-order effects are scarcely legitimate.

VII. KILLIAN'S MEASUREMENTS ON THE MERCURY POSITIVE COLUMN [13]

Killian has published a detaile dstudy of electrical conditions in a mercury discharge in a tube 6.2 cm in diameter with a constant current of 5 amps at three pressures. The precision is presumably much higher than that obtained with cæsium. The dissipation of power apart from recombination is ascribed by Killian to inelastic collisions at 4.9 volts. In Table 4 I present the essential data and the results of computations such as have been made for cæsium. The effective collision area q_{12}, computed by equation 1, is far from constant and I assume that the low-pressure value is correct and that collisions of the second kind are important at the higher pressures. In mercury there are three low-excitation potentials at 4.66, 4.86, and 5.43 volts, giving the states 2^3P_0, 2^3P_1, and 2^3P_2 of weights 1, 3, and 5. The assumption that the three states are in their equilibrium ratio leads to values of the number of excited atoms which seem unreasonably high and there are other good reasons to doubt that 2^3P_2 is populated in proportion to its weight. If most of the atoms are in $2\,P_0$ and $2\,P_1$, populated in the ratio of 1 to 3—

$$q_{21}=\frac{1}{4}\,q_{12}\left(\frac{4.9}{V_0}+1\right) \tag{15}$$

TABLE 4.—*Collisions of the first and second kind in mercury*

	0.0002 mm	0.001 mm	0.0053 mm
Atoms/cm³	0.61×10^{13}	3.1×10^{13}	16.1×10^{13}.
N_e	1.11×10^{12}	2.18×10^{12}	4.57×10^{12}.
V_e	3.27 volts	2.37 volts	1.71 volts.
$C_1\,r-C_2\,1$	0.31×10^{18}	0.96×10^{18}	1.71×10^{19}.
$q_{1\,2}$	0.68×10^{-15} cm²	(0.355×10^{-15})	(0.12×10^{-15}).
$q_{2\,1}$		0.52×10^{-15} cm²	0.66×10^{-15} cm².
Excited atoms per cm³, n_2		0.50×10^{13}	2.46×10^{13}.
Normal atoms, n_1		2.6×10^{13}	13.6×10^{13}.
Duration, τ		0.97×10^{-4} seconds	0.905×10^{-4} seconds.
Time between collisions, $\tau_{2\,1}$		2.56×10^{-4}	1.14×10^{-4}.
Duration, τ_0		1.56×10^{-4}	4.35×10^{-4}.

(Inclusion of 2^3P_2 changes ¼ to ⅑.) With this rather arbitrary assumption, the tabulated values for the number and duration of excited atoms are derived. n_2/n_1 is so high that n_1 is appreciably less than the total number of atoms. At the highest pressure the duration of excited states is nearly equal to the time between collisions of the second kind and the concentration n_2 has reached nearly its equilibrium value.

[13] Killian, Phys. Rev., vol. 35, p. 1238, 1930.

The computed value of τ_0, the duration in the absence of collisions, can be compared with direct measurements of the duration of 2^3P_0 and 2^3P_1 atoms. Couilette [14] has measured the diffusion time of 2^3P_0 atoms between concentric spheres 3.17 cm apart and finds the time 2.5×10^{-4} seconds at 0.0013 mm and 5×10^{-4} seconds at 0.0051 mm. The conditions are roughly comparable with Killian's conditions and the diffusion times are seen to be almost equal to the two values of τ_0. Measurements of the diffusion time of resonance radiation which give the duration of 2^3P_1 lead to values of the order of one-twentieth of this.[15]

The agreement between the computed values of τ_0 and the observed diffusion time of 2^3P_0 atoms implies a predominance of 2^3P_0 atoms in contradiction to my assumptions. Actually the number of atoms in 2^3P_0 must be more than a third of n_2 and the values for n_2, τ and τ_0 will be somewhat less than in Table 4. Apart from this minor complication, the results are consistent with the view that collisions of the second kind play an important part in the mercury discharge, even with low pressures and current densities.[16]

VIII. MEASUREMENTS OF KOPFERMANN AND LADENBURG ON THE NEON POSITIVE COLUMN [17]

Studies of the anomalous dispersion of excited neon give detailed information as to the concentration of different excited states under a wide range of conditions. Measurements were made on the transitions between the lower states s_3, s_4, s_5, and the various p states (Paschen notation). The lower states are analogous to the 2^3P states of mercury but in inverted order. The concentrations of these states approach constant values in the equilibrium ratios with a current density of about 0.1 amp/cm^2 for a pressure of 1 mm. Only at very low currents is there a marked preponderance of the metastable states as compared with the radiating state. With increasing pressure up to 9 mm the equilibrium is attained at lower currents in accord with the results with cæsium, but unlike cæsium the number of excited atoms decreases with increasing pressure. Only with the highest current density, 1.4 amp/cm^2, is the number of atoms in the higher states near the equilibrium value. The equilibrium value for the p states at 1 mm pressure corresponds to an electron energy $V_0 = 2$ volts while the s states correspond to values between 1.6 and 1.85 volts. Measurements of electron energies in the neon positive column[18] give values within this range for comparable conditions of pressure and current.

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[14] Coulliette, Phys. Rev., vol. 32, p. 636, 1928.

[15] Webb and Messenger, Phys. Rev., vol. 33, p. 319, 1929.

[16] Latysceff and Leipunksy, Zeits. f. Phys., vol. 65, p. 111, 1930, give direct measurements of collisions of the second kind in mercury. The demonstration of the effect is very convincing, but their estimate of the absolute value of the probability is based on an assumed value of the number of excited atoms which is certainly far too high. Their value of the probability is much lower than that deduced from Killian's measurements. Published estimates of $q_{1,2}$ cover a very wide range of values and are, in general, much less than I deduce. Killian's experimental data can not be wrong in order of magnitude and the assumptions I have used tend to give a value of $q_{1,2}$; that is, too low rather than too high.

[17] Kopfermann and Ladenburg, Zeits. f. Phys., vol. 48, pp. 15, 26, 51, and 192, 1928. Zeits. f. Phys., vol. 65, p. 167, 1930.

[18] Seeliger and Hichert, Ann. der Phys., vols. 5–11, p. 817, 1931.

IX. CONCLUSIONS

In a cæsium positive column with pressures above 0.006 mm there are simple relations between the electron temperature T_e, the number of excited atoms, n_2, and the radiation intensity. The number of excited atoms in the first excited state is nearly equal to the number which would exist in equilibrium at a temperature T_e. With increasing current T_e and n_2 slowly increase and the radiation intensity remains proportional to n_2. The electron concentration and the number of collisions of the first kind increase greatly, but the number of collisions of the second kind increase at an equal rate and the only primary effect is to reduce the life of the excited states. With increasing pressure, T_e and the concentration of excited atoms decrease while n_2 gradually increases. The radiation remains nearly constant.

The studies of Kopfermann and Ladenburg of anomalous dispersion in the neon positive column and my deductions from Killian's electrical measurements in the mercury positive column indicate that the relation between the number of excited atoms and T_e are qualitatively similar for neon, mercury, and cæsium. These atoms are extremely different in structure and one can conclude that the relation is quite general. While the approach to equilibrium concentration occurs at low current for the first excited state (or close group of states) it requires high currents to approach equilibrium in the second states. Thus there is no reason to expect a distribution of intensity in the line spectrum (in a series of lines, for instance) that is simply related to the electron temperature.

WASHINGTON, June 13, 1932.

THE AREAS AND TENSILE PROPERTIES OF DEFORMED CONCRETE-REINFORCEMENT BARS

By A. H. Stang, L. R. Sweetman, and C. Gough

ABSTRACT

In order to compute the yield point and tensile strength of a deformed reinforcement bar from tensile tests, the crosss-section area must be known. Four practical methods of measuring this area have been studied. The determination of the weight and length of a bar (assuming a density of 0.2833 lb./in.^{3}) and the measurement of the volume of liquid displaced by a bar of known length gave results about ten times as consistent as those obtained with a micrometer or a planimeter. The first method is considered the most practical.

Specifications for deformed bars permit the tests of bars which have been machined to a cylindrical cross section. Data are lacking as to the comparative tensile properties of machined and unmachined specimens. Tensile tests were therefore made on bars having the original lugs, bars from which the lugs had been filed and bars which had been machined to a cylindrical cross section. The results of these tests showed that the yield point and tensile strength were increased slightly by filing and more by machining, but that the differences were too small to warrant the cost of machining the specimens.

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I. SCOPE AND PURPOSE OF THE TESTS

Specifications [1] for deformed concrete-reinforcement bars list limiting values of the stress (lbs./in.^{2}) at the yield point and the tensile strength of the bars. When reinforcing bars are tested the load in pounds at the yield point and the maximum are observed. The stresses are then computed by dividing the load by the original cross-sectional area of the bar and compared with the values given in the specification.

[1] United States Government master specification for bars, reinforcement, concrete, Federal Specifications Board Specification No. 350a. American Society for Testing Materials standard specifications for billet-steel concrete reinforcement bars, A. S. T. M. designation: A–15–13 and standard specifications for rail-steel concrete reinforcement bars, A. S. T. M. designation: A–16–14; A. S. T. M. standards, 1930, Pt. I, Metals, pp. 131 and 135, respectively.

The specifications are drawn up for the purpose of insuring that the bars shall have adequate strength, that they shall be made of a suitable quality of material, and, in addition, that the purchaser shall not be required to pay for an undue amount of overweight in delivery. The insuring of adequate strength does not require the specification of the "yield point" or "tensile strength" of the material in the bars. This purpose would be equally well, if not better, served by making use of the principles of specifications already applied to manila and wire rope, specifying for each nominal size a "minimum yield load" and a "minimum tensile load." That, in fact, is the form in which the designer will use the specified values, regardless of the particular manner in which they are expressed in the specifications.

II. THE SPECIMENS

Deformed bars used in this country vary in size from ¼ to 1¼ inches. One-half inch and 1-inch bars, both round and square, were selected for these tests in which four types of deformation and three grades of steel were used. (See Table 1.) The rail steel bars were donated by the Buffalo Steel Co. The other bars were purchased from commercial stock.

Twenty-four bars were used in the tests. Beginning at one end of a bar, 12 test specimens were cut in sequence, A1, B1, C1, D1; A2, B2, C2, D2; A3, B3, C3, D3. The A specimens were 12 inches long, the others 20 inches. They were used as follows:

Type A, for area and density determination.

Type B, for tensile test, as received.

Type C, for tensile test after the lugs had been filed, by hand, from the middle 9-inch length.

TABLE 1.—*The bars, description and density*

Type of deformation	Grade of steel	Size	Shape	Density
		Inch		*Lbs./in.*[3]
Corrugated	Intermediate, billet	½	Round	0.2825
		½	Square	.2826
		1	Round	.2827
		1	Square	.2829
Diamond	do	½	Round	.2824
		½	Square	.2825
		1	Round	.2823
		1	Square	.2827
Havemeyer	Structural, billet	½	Round	.2827
		½	Square	.2826
		1	Round	.2825
		1	Square	.2826
	Intermediate, billet	½	Round	.2823
		½	Square	.2822
		1	Round	.2822
		1	Square	.2827
	Hard, billet	½	Round	.2824
		½	Square	.2827
		1	Round	.2825
		1	Square	.2827
Rail	Hard, rail	½	Round	.2820
		½	Square	.2823
		1	Round	.2824
		1	Square	.2825

Type D, for tensile test after having been machined for the middle 9-inch length to the largest cylindrical section possible with removal of all scale.

III. DETERMINATION OF AREA

The area determinations by the different methods were made only on the type A specimens of the rail steel bars. These specimens had relatively small deformations and were more regular in cross section than some of the other bars.

1. WEIGHT-LENGTH METHOD

By this method the area generally is calculated from the weight of a measured length of the bar on the assumption that a steel bar 1 square inch in section and 1 foot long weighs 3.400 pounds, or 0.2833 lb./in.^{3} This value for the density is given in all American handbooks. To check the accuracy of this value, the density of one specimen of each type of deformation, grade of steel, and size was determined by the capacity and density section of the bureau. These densities, given in Table 1, are all within one-half of 1 per cent of the nominal density of 0.2833 lb./in.^{3} The average density, 0.2825 lb./in.^{3}, is less than 0.3 per cent from the nominal value.

The weight-length method is obviously an indirect volume measurement and the areas obtained represent average rather than minimum cross sections.

For this investigation each of three observers measured the length of the bars with a steel scale graduated to 0.01 inch and weighed them on an equal arm balance to the nearest 0.001 pound. Areas were then calculated by the following formula

$$A=\frac{W}{\rho L}$$

where

A is the area, square inch.
W is the weight, pound.
L is the length, inch.
ρ is the density, pounds per cubic inch.

The areas calculated by this method are given in Table 2. This table also lists the deviation of each observation from the average.

2. IMMERSION METHOD

For this method the specimens were immersed in denatured alcohol contained in a cylindrical glass graduate and the areas given in Table 2 were computed by the formula

$$A=\frac{V_1-V}{16.39L}$$

where

A is the cross-sectional area of the specimen, square inch.
V is the graduate reading before the specimen is immersed, cubic centimeter.
V_1 is the graduate reading after the specimen is immersed, cubic centimeter, and
L is the length of the specimen.

The length, L, was determined in the same way as for the weight-length method. This method has been recommended by Scheirer.[2]

[2] Accurate Method for Determining Actual Areas for Deformed Steel Reinforcing Bars, M. K. Scheirer, Concrete, vol. 33, p. 24, September, 1928.

TABLE 2.—*Cross-sectional area of deformed bars*

[Deformed rail steel concrete-reinforcement bars, type A specimens]

Nominal size (inch)	Shape	Specimen No.	Observer	Weight-length method		Immersion method		Micrometer method		Planimeter method	
				Area	Deviation	Area	Deviation	Area	Deviation	Area	Deviation
				Square inch	*Per cent*	*Square inch*	*Per cent*	*Square inch*	*Per cent*	*Square inch*	*Per cent*
½	Round	1	1	0.1904	0.11	0.1898	0.05	0.1901	2.87	0.183	1.67
			2	.1899	.16	.1898	.05	.1855	.38	.180	.00
			3	.1903	.05	.1900	.05	.1787	3.30	.177	1.67
			Average	.1902		.1899		.1848		.1800	
½	do	2	1	.1907	.16	.1911	.00	.1909	1.49	.190	1.77
			2	.1902	.11	.1910	.05	.1847	1.81	.183	1.98
			3	.1904	.00	.1911	.00	.1886	.27	.187	.16
			Average	.1904		.1911		.1881		.1867	
½	do	3	1	.1886	.05	.1890	.21	.1901	2.04	.183	1.10
			2	.1883	.11	.1895	.05	.1863	.00	.177	2.21
			3	.1885	.00	.1896	.11	.1825	2.04	.183	1.10
			Average	.1885		.1894		.1863		.1810	
½	Square	1	1	.2559	.04	.2560	.12	.2549	.12	.250	1.92
			2	.2559	.04	.2568	.20	.2539	.27	.243	.94
			3	.2561	.04	.2561	.08	.2549	.12	.243	.94
			Average	.2560		.2563		.2546		.2453	
½	do	2	1	.2555	.16	.2559	.16	.2549	.12	.250	.93
			2	.2546	.20	.2554	.04	.2539	.27	.243	1.90
			3	.2552	.04	.2551	.16	.2549	.12	.250	.93
			Average	.2551		.2555		.2546		.2477	
½	do	3	1	.2541	.04	.2553	.04	.2529	.28	.250	.00
			2	.2539	.04	.2550	.08	.2539	.12	.250	.00
			3	.2541	.04	.2553	.04	.2539	.12	.250	.00
			Average	.2540		.2552		.2536		.2500	
1	Round	1	1	.764	.04	.767	.00	.754	.40	.743	.04
			2	.764	.04	.767	.00	.757	.00	.737	.85
			3	.765	.09	.767	.00	.760	.40	.750	.90
			Average	.7643		.7670		.7570		.7433	
1	do	2	1	.765	.00	.768	.04	.776	.82	.757	.17
			2	.765	.00	.768	.04	.762	1.00	.753	.36
			3	.765	.00	.769	.09	.771	.17	.757	.17
			Average	.7650		.7683		.7697		.7557	
1	do	3	1	.766	.00	.768	.13	.767	.88	.760	.30
			2	.766	.00	.769	.00	.760	.04	.753	.62
			3	.766	.00	.770	.13	.754	.83	.760	.30
			Average	.7660		.7690		.7603		.7577	
1	Square	1	1	.979	.07	.979	.03	.967	.21	.970	.45
			2	.978	.03	.978	.07	.961	.41	.967	.13
			3	.978	.03	.979	.03	.967	.21	.960	.59
			Average	.9783		.9787		.9650		.9657	
1	do	2	1	.975	.07	.975	.03	.963	.13	.957	.28
			2	.974	.03	.975	.03	.959	.55	.943	1.18
			3	.974	.03	.974	.07	.971	.69	.963	.91
			Average	.9743		.9747		.9643		.9543	
1	do	3	1	.981	.00	.981	.07	.973	.28	.960	.24
			2	.981	.00	.981	.07	.967	.34	.960	.24
			3	.981	.00	.983	.13	.971	.07	.953	.49
			Average	.9810		.9817		.9703		.9577	
			Grand average		.05		.07		.64		.77

The bars were held by a small copper wire, the immersed volume of which was less than 1/20 cm^3. Alcohol was used rather than water because, due to its lower surface tension, the level of the liquid in the graduate could be more accurately determined. It also wets the steel bar so that air bubbles are not trapped on the surface as with water. The calibrated graduate used with the ½-inch bars was graduated to 0.5 ml and that used with the 1-inch bars to 1.0 ml. On both readings were estimated to 1/10 ml.

3. MICROMETER METHOD

The minimum areas were calculated from measurements with a micrometer caliper of the sides of the square bar or the diameter of round bars. Two measurements to the nearest 0.001 inch were taken on each side of two sides (or of two diametral planes perpendicular to each other) and the four measurements were averaged. Correction was made for the rounded corners of the square bars, the radii of these corners being measured with radius gages. The areas are given in Table 2.

4. PLANIMETER METHOD

The smooth end of a bar was impressed on a paper and the area of the impression measured with a polar planimeter. It is customary in some laboratories to ink the end of the bar, and force it, using a testing machine, against the paper which may be backed up with blotting paper or some other relatively soft substance. Preliminary studies with round and square machined specimens showed that this procedure gave areas smaller than the area computed from the dimensions. This difference was probably due to the soft backing material.

The method finally adopted was as follows: The end of the bar was finished smooth, care being taken to avoid rounding the corners. This surface was inked with an inking pad, the surplus ink around the edges wiped off, and several impressions were made on buff detail paper. The weight of the specimen, 12 inches long, supplied the impressing force. The second or third impression was usually better than the first due to the smaller amount of ink on the end of the bar. This method resulted in clear cut perimeters.

The areas were measured with a Coradi polar planimeter with an arm length such that each division of the vernier amounted to 0.01 $in.^2$. The mean of three measurements by each observer is given in Table 2.

5. COMPARISON OF THE DIFFERENT METHODS

The deviations given in Table 2 are measures of the variation in the areas as determined by different observers and by different methods. If the average of the deviations for one method is smaller than for another method, it is probable that the first method will give more consistent values for different observers than the second. On this basis, the weight-length method is best and then come, in order, the immersion method, the micrometer method, and finally the planimeter method.

This rating is supported by a consideration of the observational errors involved. If three sets of observations made by the weight-length method are not in error more than plus or minus 0.01 inch in

12 inches as regards length and not more than plus or minus 0.001 pound in 0.668 pound as regards weight (½-inch round bar), then the average departure of an individual determination from the mean of three should never exceed 0.2 per cent. For the immersion method, with the same uncertainty as regards length and a possible error of plus or minus 0.1 ml in 38.7 ml in measuring the displacement, the average departure should not exceed 0.3 per cent; while in the planimeter method with an uncertainty of 0.01 in.^{2} in the measurement of an area of only 0.2 in.^{2}, the average departure of three determinations from the mean may reach 4.3 per cent. While these percentages are limiting values (not the most probable average deviation) they should conform approximately in relative magnitude with the grand averages of the observed deviations in Table 2. Considering the methods in the order discussed, the computed relative magnitudes of the deviations for the three methods are 1:1.5:21, while the relative magnitudes of the corresponding observed deviations are 1:1.4:15.

A similar analysis of the micrometer method was not attempted. Deformed bars do not have simple regular sections, and the cross sectional area may vary from point to point along the bar, so that the average deviation depends more upon the location of the measuring stations on the bar than upon the precision of the micrometer readings.

Current specifications permit the deliveries of reinforcement bars one-half inch in diameter or larger which deviate not more than plus or minus 7.5 per cent from the nominal area. If the nominal area is used in the determination of yield point, tensile strength and elongation from the values observed during a tensile test, errors of this order of magnitude may be introduced in the results. If an accuracy of this order of magnitude is sufficient to insure that the material is of suitable quality without an undue percentage of rejections of borderline material, it would be simplest and most economical to require that yield points and tensile strengths for specification purposes be calculated on the basis of the nominal areas, which are used by the engineer in his design calculations.

If an accuracy of this order is not considered sufficient to insure that the material is of suitable quality without undue rejections of borderline material, the weight-length method of area measurement is undoubtedly to be preferred to any of the others. It requires no special apparatus, the measurements are easy to make, and the errors (maximum plus or minus 0.2 per cent) are much below those tolerated (plus or minus 1 per cent) in testing machines.

IV. THE TENSILE TESTS

1. METHOD OF TESTING

The ½-inch bars were tested in a testing machine having 50,000 pounds capacity and the 1-inch bars in a testing machine having a capacity of 100,000 pounds. The specimens were held with wedge grips, well lubricated with grease and graphite on the sliding surfaces. The rate of separation of the heads of both machines under no load, was 0.4 inch per minute. The yield point was determined by the drop of beam. All specimens had definite drop of beam yield points.

2. CALCULATION OF RESULTS

The yield point and tensilve strength values were calculated from the test loads for the different types of tensile specimens by dividing by the area found as follows:

Type B specimens tested as received.—The areas were determined by the weight-length method.

Type C specimens with lugs filed off.—The specimens were weighed and their length measured. The fractional length with lugs left on was then determined from a count of the total number of original lugs and of the lugs left on. The weight of this length was determined from the calculated weight of an equal length of the corresponding A specimens. The difference between the total weight of the C specimen and the weight of the fractional length with lugs left on gave the weight of the fractional length from which the lugs had been filed. The area was then calculated by the weight-length method.

Type D specimens, machined to a cylindrical section.—The diameter was measured to the nearest 0.001 inch with a micrometer caliper and the area calculated from this diameter.

The elongation in 8 inches was measured with dividers and a steel scale to 0.01 inch. For the few specimens which broke outside of the middle half of the gage length, the elongation was computed according to the method outlined in A. S. T. M. tentative specification, serial designation: E8–27T.[3]

3. AVERAGE RESULTS

The yield-point and tensile-strength values for the three specimens of each type from each bar were very consistent. The elongation values varied more. The greatest variation of a single value from the mean for each of the 72 groups of three specimens was less than 3½ per cent for the yield point values and less than 2½ per cent for the tensile strengths (except for one group). For 54 of the groups the maximum deviation of the elongation values was less than 5 per cent. The average results are given in Table 3, each value for yield point, tensile strength and elongation being the average for the three similar specimens from each bar.

[3] Tentative Methods of Tension Testing of Metallic Materials, Proc. A. S. T. M., vol. 27, Pt. I, p. 1078.

TABLE 3.—*Average results of tensile tests of concrete reinforcement bars*

Type of deformation	Grade of steel	Size of bar	Shape	Yield point			Ratio of yield points		Tensile strength			Ratio of tensile strengths		Elongation in 8 inches			Ratio of elongation	
				Type B as received	Type C lugs filed off	Type D cylindrical section	C/B	D/B	Type B as received	Type C lugs filed off	Type D cylindrical section	C/B	D/B	Type B as received	Type C lugs filed off	Type D cylindrical section	C/B	D/B
		Inch		*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*			*Lbs./in.²*	*Lbs./in.²*	*Lbs./in.²*			*P. ct.*	*P. ct.*	*P. ct.*		
Corrugated	Intermediate billet	½	Round	48,300	49,300	49,300	1.02	1.02	72,200	73,100	73,900	1.01	1.02	23.7	23.3	24.6	0.98	1.04
		½	Square	43,700	45,200	44,900	1.03	1.03	73,300	75,300	75,900	1.03	1.04	21.5	23.8	22.7	1.11	1.06
		1	Round	48,500	48,800	51,500	1.01	1.06	82,600	82,800	84,200	1.00	1.02	23.7	22.4	22.3	.95	.94
		1	Square	39,600	40,200	40,200	1.02	1.02	70,100	71,100	73,000	1.01	1.04	26.7	27.6	26.9	1.03	1.01
Diamond	Intermediate billet	½	Round	46,100	47,100	47,500	1.02	1.03	70,400	71,500	72,900	1.02	1.04	24.7	24.5	22.2	.99	.90
		½	Square	55,200	56,100	58,200	1.02	1.05	83,300	84,500	85,800	1.01	1.03	22.4	21.7	19.5	.97	.87
		1	Round	50,300	50,300	53,100	1.00	1.06	72,300	72,600	73,100	1.00	1.01	28.3	28.4	28.2	1.00	1.00
		1	Square	39,700	40,100	42,700	1.01	1.08	68,700	69,600	70,300	1.01	1.02	29.2	28.2	28.4	.97	.97
	Structural billet	½	Round	41,700	42,300	43,600	1.01	1.05	57,500	57,600	59,500	1.00	1.03	29.9	27.9	28.1	.93	.94
		½	Square	41,900	43,700	42,100	1.04	1.01	59,200	60,700	61,300	1.03	1.04	22.4	27.0	27.2	1.20	1.21
		1	Round	38,200	38,100	38,700	1.00	1.01	58,300	58,800	59,200	1.01	1.02	31.8	32.1	31.5	1.01	.99
		1	Square	38,400	39,100	40,500	1.02	1.06	60,600	61,000	61,700	1.01	1.02	31.9	31.7	30.5	.99	.96
Havemeyer	Intermediate billet	½	Round	52,400	52,500	52,300	1.00	1.00	77,000	77,800	78,200	1.01	1.02	22.8	22.0	21.9	.97	.96
		½	Square	48,400	50,100	49,000	1.03	1.01	70,900	71,500	72,100	1.01	1.02	26.1	25.4	24.2	.97	.93
		1	Round	47,600	47,600	48,200	1.00	1.01	77,900	78,400	78,800	1.01	1.01	25.6	26.2	25.3	1.02	.99
		1	Square	43,500	45,100	46,200	1.04	1.06	73,500	75,100	75,200	1.02	1.02	26.4	26.6	25.9	1.01	.98
	Hard billet	½	Round	53,200	53,000	52,500	1.00	.99	80,900	81,600	82,000	1.01	1.01	20.1	21.5	21.5	1.07	1.07
		½	Square	52,400	53,100	53,700	1.01	1.02	89,200	89,900	91,600	1.01	1.03	16.9	16.5	17.4	.98	1.03
		1	Round	51,900	51,800	51,500	1.00	.99	88,000	88,100	88,200	1.00	1.00	22.5	21.2	22.1	.94	.98
		1	Square	50,300	50,700	51,200	1.01	1.02	85,900	86,500	87,300	1.01	1.02	21.3	20.7	21.9	.97	1.03
Rail	Hard rail	½	Round	59,100	59,500	60,800	1.01	1.03	92,300	92,700	95,600	1.00	1.04	15.3	16.3	17.0	1.07	1.11
		½	Square	66,200	65,900	66,900	1.00	1.01	100,100	100,300	102,200	1.00	1.02	13.8	15.9	17.6	1.15	1.28
		1	Round	57,200	57,300	58,800	1.00	1.03	98,100	98,700	99,900	1.01	1.02	18.6	19.5	18.3	1.05	.98
		1	Square	48,800	49,000	49,200	1.00	1.01	80,400	81,100	82,200	1.01	1.02	23.2	23.8	22.8	1.03	.98

THE EFFECT OF FILING OFF THE LUGS, ON THE TENSILE STRENGTH

The average maximum load in pounds of the type C specimens with lugs filed off was less in all cases than the average maximum load in pounds of the type B specimens which were tested as received. The areas based upon weight-length measurements were also less, but Table 4 which lists the decrease in maximum load and area of the type C specimens with respect to the type B specimens shows that the decrease in area was in all cases greater than the decrease in maximum load. The lugs were therefore effective in resisting tensile forces to some extent. An example will be used to show how the relative effectiveness of the area of the lugs in tension as given in Table 4 has been calculated.

Example.—½-inch round bars, Havemeyer type of deformation, intermediate grade of billet steel:

Type of specimen	Average area	Average tensile load	Average tensile strength
	Square inch	*Pounds*	*Lbs./in.* ^{2}
B, as received	0.1935	14,910	77,000
C, lugs filed off	.1880	14,630	77,800
B–C	.0055	280	

$$\text{Tensile strength of lug area, } \frac{280}{0.0055} = 50{,}900 \text{ } lbs./in.^2$$

$$\frac{\text{Tensile strength of lug area}}{\text{Tensile strength for Type C}} = \frac{50{,}900}{77{,}800} = 0.65$$

It may, therefore, be concluded that the lug area of these bars was 65 per cent effective in resisting tensile stresses. Similar values for all bars are given in Table 4. Since these values depend on small differences between relatively large numbers, the results are somewhat variable. They show, however, that the lug area of the Havemeyer and rail steel bars were more than 50 per cent effective in resisting tensile forces. These lugs were parallel to the axis of the bars. The corrugated and diamond deformations were not parallel to the axis of the bars and the lug area was less effective in resisting tensile forces than for the other types. Since, however, the lug areas in the Havemeyer bars were always much larger than in the other types of bars (see Table 4) the effectiveness of the total area in resisting tensile load was practically the same for all types of bars as shown in C/B ratios of Table 3.

TABLE 4.—*Effect of filing off lugs on the maximum load and on the area*

Type of deformation	Grade of steel	Nominal size	Shape	Decrease in maximum load	Decrease in area	Relative effectiveness of area of lugs in tension
		Inch		*Per cent*	*Per cent*	*Per cent*
Corrugated	Intermediate	½	Round	0.9	2.1	
		½	Square	1.0	3.7	
		1	Round	.6	.9	
		1	Square	.7	2.0	
Diamond	do	½	Round	.4	1.8	
		½	Square	.9	2.4	
		1	Round	.9	1.4	
		1	Square	1.1	2.5	
Havemeyer	Structural	½	Round	2.6	2.7	
		½	Square	6.1	8.3	
		1	Round	1.7	2.7	
		1	Square	4.4	5.0	
	Intermediate	½	Round	1.9	2.8	
		½	Square	5.3	6.2	
		1	Round	2.4	2.7	
		1	Square	4.3	6.4	
	Hard	½	Round	2.1	2.9	
		½	Square	5.4	6.1	
		1	Round	3.1	3.2	
		1	Square	3.6	4.3	
Rail	do	½	Round	1.8	2.2	
		½	Square	2.3	2.4	
		1	Round	1.0	1.5	
		1	Square	1.1	2.0	

5. COMPARISON OF TENSILE PROPERTIES OF UNMACHINED AND OF MACHINED BARS

Table 3 gives the average results of the tensile tests. The tensile strength of type D specimens machined to cylindrical cross section was in all cases greater than that of the type C specimens, with lugs filed off. The increase in average strength of the type D specimens over the type B specimens was, however, in all cases less than 5 per cent.

The same general conclusions can be drawn from the yield point values although in two instances the average yield point for the type D specimens was 1 per cent below the value for the type B specimens.

The effect of type of specimens on the elongation was erratic. On the average, the elongation was not much affected by filing off the lugs or machining the bar. The average elongation in 8 inches was 23.7 per cent for the bars tested as received, 23.9 per cent for the bars from which the lugs had been filed and 23.7 per cent for the bars which were machined to a cylindrical cross section.

Table 3 shows that the tensile properties are not influenced by the size or shape of the bar, or by the type of deformation.

The small difference in the tensile properties of machined and unmachined specimens leads to the suggestion that the use of the expensive machined specimen be eliminated from the specifications. If the use of the original sections of deformed bars were made mandatory for tensile tests, one point of controversy would be eliminated.

The results listed in Table 3 show only two border-line cases in which specimens which failed to comply with the requirements of the specification as to yield point or tensile strength when tested as

received, did comply when machined. These are the 1-inch square corrugated and diamond bars. For the intermediate grade of steel, the specified minimum yield point and tensile strength values are 40,000 and 70,000 lb./in.^{2}, respectively.

6. DETERMINING WHETHER A SPECIMEN CONFORMS TO THE REQUIREMENTS OF THE SPECIFICATION

By chance, the tensile strength of the 1-inch square rail steel specimen B–3, tested as received, affords an example of the difficulties of determining whether a specimen conforms to the requirements of the specification, when no method of area determination has been specified. Table 5 gives data as to the breaking load of this bar, of the area as determined by different methods (average results from Table 2 have been used), and of the tensile strength, when computed with regard to the different areas.

In this case, the values given in Table 5 show that the tensile strength computed by the nominal area, weight-length, and immersion methods, did not conform to the requirements of the specification. The tensile strength, computed from areas determined by the micrometer and planimeter methods, did comply with the specified requirement. In border-line cases such as this, it is apparent that much confusion results and honest differences of opinion arise when the method of area determination is not specified. The necessity of specifying some method of area determination is obvious.

TABLE 5.—*The tensile strength of rail steel specimen B–3, 1 inch square, tested as received*

[Breaking load, 77,970 pounds]

Method of determining area	Area	Tensile strength
	Square inch	*Lbs./in.*^{2}
Nominal area	1.000	77,970
Weight-length	.9780	79,700
Immersion	.9767	79,800
Micrometer	.9703	80,300
Planimeter	.9577	81,400
Specified minimum		80,000

V. CONCLUSIONS

1. Area determinations by different observers of deformed concrete-reinforcement bars, one-half and 1 inch in size, both round and square in section were made by four different methods. The conclusions reached as a result of this study are as follows:

(*a*) If specifications for concrete-reinforcing bars specify the yield point and tensile strength in pounds per square inch of the material in the bars, the method of determining the area to be used in calculating them should be definitely specified.

(*b*) The nominal areas which are used by the engineer in his design calculations should be used in computing yield point and tensile strength values from the test results if the accuracy of the nominal area is considered sufficient. Since current specifications permit the deliveries of reinforcement bars one-half inch in diameter or larger which deviate not more than plus or minus 7½ per cent from the nominal area, errors of this order of magnitude may be introduced in the results.

(*c*) If accuracy of the order of plus or minus 7.5 per cent in the determination of yield point, tensile strength, and elongation of concrete reinforcement bars is not sufficient to insure that the material is of suitable quality, without an undue percentage of rejections of border-line material, the specifications should require the use of the weight-length method.

(*d*) The immersion method under ordinary laboratory conditions gives no greater accuracy than the weight-length method, and is much less easy to apply.

(*e*) The micrometer method applied to deformed bars gives much less accurate results than either the weight-length or the immersion method.

(*f*) The planimeter method is costly and time consuming. With the usual planimeters and within the usual range of sizes it gives much less accurate results than either the weight-length or the immersion method.

2. Tensile tests were made of deformed concrete-reinforcement bars, of three grades of steel, four types of deformation, one-half and 1 inch in size, both round and square in section. Each bar was tested (1) in the original condition, (2) after the lugs had been filed by hand from the middle 9-inch length, and (3) after the bars had been machined to a cylindrical cross section for the middle 9-inch length. The conclusions reached as a result of the tensile test are as follows:

(*a*) Removing the lugs from deformed concrete-reinforcement bars decreased slightly the load (pounds) carried by the bars at the yield point and at failure. The percentage decrease in load, however, was in no case as large as the percentage decrease in the average area as determined by the weight-length method, so that the yield point (pounds per square inch) increased from 0 to 4 per cent and the tensile strength (pounds per square inch) from 0 to 3 per cent, with no significant difference between the different types of bars.

(*b*) There was, however, a marked difference in the manner in which the different types of lugs contributed to the strength of the bar. The area of the Havemeyer lugs was approximately 50 per cent effective in resisting tensile stresses, while the areas of the corrugated and diamond type lugs were less effective.

(*c*) Machining deformed concrete-reinforcement bars to a cylindrical cross section increased the tensile strength (pounds per square inch) over the tensile strength of similar bars tested with the lugs on. The increase was, however, in no case as large as 5 per cent.

(*d*) The yield point (pounds per square inch) of deformed concrete-reinforcement bars machined to a cylindrical section was in general greater than the yield point of similar bars not machined. The maximum increase was 8 per cent.

(*e*) The effect of machining deformed concrete-reinforcement bars on the elongation was small and erratic. Sometimes the machined bars showed higher elongation and sometimes lower. The maximum difference for the elongation of unmachined and machined bars was less than 5 per cent in 8 inches. In the specimens tested, the difference was in no case sufficient to cause rejection of the material in the unmachined condition.

(*f*) These differences seem to be altogether too small to warrant the cost of machining concrete-reinforcement bars when testing under specifications.

WASHINGTON, August 1, 1932.

A CALORIMETRIC METHOD FOR DETERMINING THE INTRINSIC ENERGY OF A GAS AS A FUNCTION OF THE PRESSURE

By Edward W. Washburn

ABSTRACT

If a known mass of gas compressed in a bomb at a known pressure be immersed in a calorimeter and allowed to expand slowly to atmospheric pressure, the cooling effect can be compensated by electrical heating. Since the external work is accurately known, a precision discussion shows that the method should yield an accurate value ($\pm < 1$ cal. for a liter bomb) for the accompanying change, ΔU, in the internal or intrinsic energy of the gas. In order to obtain reliable results, the energy effects associated with the changes in stress on the walls of the bomb must be corrected for or reduced to a negligible amount by proper bomb design. From the standpoint of simplicity, rapidity, and accuracy the method is probably superior to any other means of determing this quantity.

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I. NOMENCLATURE

B Barometric pressure.
C_p Heat capacity at constant pressure.
j Joule.
M Molecular weight.
m Mass.
p Pressure.
Q Quantity of heat.
R Gas constant per mole.
T Absolute temperature.
t Centigrade temperature.
U Intrinsic energy.
v Volume.
W Work.
α Linear coefficient of thermal expansion.
μ Joule-Thomson coefficient.

II. INTRODUCTION

For any system whose thermodynamic condition is determined solely by temperature and pressure, the first law of thermodynamics assumes the form

$$dU = dQ - pdv \tag{1}$$

in which U is the so-called "total," "internal," or "intrinsic" energy of the system, Q is the heat added to it, p is the pressure upon it, and v is its volume.

For any elastic system the above relation when combined with the second law yields the familiar thermodynamic equation

$$-\left(\frac{\partial U}{\partial p}\right)_T = p\left(\frac{\partial v}{\partial p}\right)_T + T\left(\frac{\partial v}{\partial T}\right)_p \tag{2}$$

in which T is the absolute temperature.

The integral of this equation, $U_T = f(p)$ for a gaseous system at the temperature T, is the quantity sought. Aside from its general thermodynamic importance this quantity is of practical interest in connection with bomb calorimetry where a knowledge of its value for oxygen and for mixtures of oxygen with carbon dioxide is needed in order to evaluate the changes in the heat content of these gases with the pressure.

III. METHODS OF EVALUATING $U_T = f(p)$

1. THE p–v–T METHOD

By operating upon an appropriate equation of state, the right-hand member of equation (2) can be obtained as a pressure function with numerical coefficients and the equation can then be integrated. In practice this method suffers from the disadvantage that there are very few gases for which p–v–T data are known with sufficient accuracy, and the acquisition of such data is a difficult and tedious undertaking.

In the absence of more exact information, it is however, convenient to remember that as a first approximation for moderate pressures the following equation, obtained by operating upon the Beattie-Bridgeman equation of state, [1] may be employed

$$-\Delta U\Big]_0^p = \left(\frac{A_0}{RT} + \frac{3c}{T^3}\right)p \tag{3}$$

in which A_0 and c are constants appearing in the equation of state.

2. THE ADIABATIC JOULE-THOMSON METHOD

In this method $\left[\frac{\partial(pv)}{\partial p}\right]_T$ is evaluated as a pressure function with the aid of measured pv values at the temperature T or, failing these, with the aid of an equation of state, and $\left(\frac{\partial U}{\partial p}\right)_T$ is obtained from the thermodynamic relation

$$-\left(\frac{\partial U}{\partial p}\right)_T = \mu C_p + \left[\frac{\partial(pv)}{\partial p}\right]_T \tag{4}$$

[1] J. A. Beattie, Phys. Rev., vol. 32, p. 699, 1928.

in which μ is the Joule-Thomson coefficient and C_p the heat capacity at constant pressure. Both μ and C_p are pressure functions.

This method also suffers from the disadvantage that reliable μ values are available only for two or three gases and the technic of obtaining them is exceedingly difficult. From the standpoint of attainable accuracy, however, the method is perhaps superior to the p-v-T method, especially at temperatures remote from room temperature.

3. THE ISOTHERMAL JOULE-THOMSON METHOD

This method differs from the preceding one only in that the product, μC_p, is determined calorimetrically by supplying measured electrical energy at such a rate as to compensate for the temperature drop which occurs in the classical Joule-Thomson experiment. The experimental technic of this "isothermal porous-plug experiment" has only recently been developed to the point where the method gives promise of yielding valuable and reliable results.[2]

4. THE DIRECT CALORIMETRIC METHOD

Since ΔU is an energy quantity, the method of measuring it directly with the aid of a calorimeter would at first sight appear to be the most convenient and accurate one to employ. With the exceptions noted below, however, attempts to employ this method have failed to give results of sufficient accuracy. The chief difficulty appears to arise from the energy effects associated with the changes in stress on the walls of the containing vessel.

One simple method of carrying out the calorimetric determination is to determine

$$Q=\int_p^B \left(\frac{\partial U}{\partial p}\right)_T dp + W = \Delta U]_p^B + B\Delta v \qquad (5)$$

where $B\Delta v$ is the work done against the atmosphere when the gas contained in a bomb is allowed to expand isothermally from the initial pressure p to the barometric pressure B, or in general to any low pressure P such that for all lower pressures the integral $\int_p^o \left(\frac{\partial U}{\partial p}\right)_T dp$ is calculable or is negligibly small.

In this form the method has been used by Douglas [3] to determine the total energy change accompanying the evaporation of a liquefied gas, and by Bennewitz and Andreewa [4] to determine U as a function of p for gases in the neighborhood of the critical point. In both of these investigations the value of ΔU was a comparatively large quantity, and great refinement of calorimetric technic was not required in order to obtain a fair percentage accuracy. For temperatures far above the critical temperature, however, ΔU is a small quantity, calorimetric technic of high precision is required and the contribution of the containing vessel to the total heat effect can not be ignored.

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[2] See (a) F. G. Keyes and S. C. Collins, Proc. Nat. Acad. Sci., vol. 18, p. 328, 1932; (b) A. Eucken, K. Clusius, and W. Berger, Z. tech. Physick, vol. 13, p. 267, 1932.

[3] Douglas, Phil. Mag., vol. 18, p. 159, 1909.

[4] Bennewitz and Andreewa, Z. physik. Chem., vol. 142A, p. 37, 1929.

IV. THE CALORIMETRIC TECHNIC

The gas to be investigated, compressed into a suitable bomb, is immersed in a constant temperature bath at the temperature T. When temperature equilibrium has been established, the pressure p in the bomb is measured, the valve is closed, the bomb is removed from the bath and weighed to determine the mass of the contained gas. The bomb is then transferred to the calorimeter and its outlet connected to a long coil of metal tubing which is likewise immersed in the calorimeter. When equilibrium has been established in the calorimeter, observations are started and the time-temperature fore-period accurately established. The valve of the bomb is now opened gradually and the gas escapes through the long coil, which is so designed as to bring the gas to the calorimeter temperature and to barometric pressure before it escapes into the atmosphere. Coincident with this operation and throughout its course, measured electrical energy is added to the calorimeter at such a rate as to maintain the temperature constant. When the pressure in the bomb has fallen to atmospheric, the electrical heat is cut off and the calorimetric after-period is accurately determined. The heat, Q, of the process is now calculable as is also the work done against the atmosphere, and from equation (5) the quantity $\Delta U]_B^p$ is then obtained.

The contribution of the bomb itself to the observed heat effect can, for a properly designed bomb, be computed as explained below or it may be eliminated by standardizing the operation with a gas for which accurate ΔU values are available.

V. THE ENERGY CONTENT OF THE BOMB AS A FUNCTION OF THE PRESSURE

The bomb itself is an elastic system and its intrinsic energy changes with the tension on its walls. Unlike the gas, however, it may not return promptly to its original energy state on release of the tension, but instead may exhibit a lag.

For this reason it is desirable (1) to design a bomb for which the change of intrinsic energy with pressure shall be as small as possible, and (2) to suitably anneal the bomb and to age it by subjecting it to a number of cycles of extension and contraction by repeated filling and emptying with compressed gas.

Since the bomb is itself an elastic system the following thermodynamic relation analogous to equation (2) is applicable

$$\left(\frac{\partial U}{\partial p_b}\right)_T = p_b\left(\frac{\partial v_i}{\partial p_b}\right)_T - B\left(\frac{\partial v_e}{\partial p_b}\right)_T + T\left(\frac{\partial v_i}{\partial T}\right)_{p_b} \tag{6}$$

in which p_b is the internal pressure, v_i the internal volume, B the constant external barometric pressure, and v_e the exterior or bulk volume. Assuming the approximations

$$\left(\frac{\partial v_i}{\partial p_b}\right)_T = \left(\frac{\partial v_e}{\partial p_b}\right)_T \text{ and } \frac{1}{v_i}\left(\frac{\partial v_i}{\partial T}\right)_{p_b} = 3\alpha$$

both independent of the pressure, and integrating gives

$$\Delta U]_B^{p_b} = \frac{(p_b - B)^2}{2}\left(\frac{\partial v_i}{\partial p_b}\right)_T + 3\alpha v_i T(p_b - B) \tag{7}$$

in which α is the linear coefficient of thermal expansion of the material composing the bomb.

For a cylindrical steel bomb with hemispherical ends, a wall thickness of 1.65 mm and a capacity of about 1 l, $\left(\frac{\partial v_e}{\partial p_b}\right)_{300°K.}$ was found to be constant and equal to 39×10^{-6} l/atm., for stresses well within the elastic limit.

For $p_b = 50$ atm. and $B = 1$ atm. we have therefore at 300°K.

$$\Delta U]_1^{50} = \frac{49^2}{2}\times39\times10^{-6} + 3\times11\times10^{-6}\times1\times300\times49 \text{ l-atm.} \quad (8)$$

$$= 4.74 + 49.16 = 53.9 \text{ j} \quad (9)$$

If the contained gas is air at 50 atm. it will give $-\Delta U]_1^{50} = 560$ j approximately. The contribution of the bomb therefore amounts to about 10 per cent of intrinsic energy change of the gas and, if the bomb is slow in returning to its original energy state, its contribution can not in practice be calculated with sufficient accuracy.

Now the first term in equation (9) is a work term, and the quantity $\left(\frac{\partial v_e}{\partial p_b}\right)_T$ can be directly measured with sufficient accuracy by immersing the filled bomb in a constant-temperature volumeter and releasing the pressure. For a steel bomb no appreciable lag is observed in this quantity. The lag therefore affects only the second term which is the larger of the two. This term can be materially reduced by constructing the bomb of a material having a low coefficient of thermal expansion. Thus if a suitable invar steel is selected for this purpose, equation (9) for the same conditions becomes

$$\Delta U]_1^{50} = 4.74 + 4.92 = 9.7 \text{ j} \quad (10)$$

The total bomb contribution will now be only 1.7 per cent of the gas effect and that part of it which is affected by lag will be less than 1 per cent and the uncertainty arising from the lag will be a negligible quantity in comparison with the other errors of measurement.

VI. EFFECTS OF ADSORPTION

In all experimental work involving p–v–T or energy relations of gases the influences of adsorbed gas on the walls of the containing vessel must be considered. These influences are usually measured and eliminated by a series of experiments with different areas of exposed surface in contact with the gas. In the present instance such experiments can be readily made by placing wire or foil (of the same material as the bomb) inside the bomb in order to increase the area of metal surface exposed. Since, however, in the present method the pressure of the gas does not fall below atmospheric during the experiment, the adsorbed gas which leaves the walls of the bomb is only the small and probably negligible amount which becomes adsorbed when the pressure is raised from 1 atmosphere to the initial pressure p_b.

VII. THE TEMPERATURE COEFFICIENT OF U_T

For correcting the calorimetric determinations to a common temperature or for reducing a measured value at one temperature to a neighboring other temperature, it is convenient to remember that the small temperature coefficient can be approximately obtained by differentiating equation (3) which gives

$$\frac{100\ d(\Delta U)}{\Delta U\ dt}=\frac{-100}{T}\left[1+6c\ T^3\left(\frac{A_0}{RT}+\frac{3c}{T^3}\right)\right] \tag{11}$$

Thus for O_2 at 25° C. this equation gives 0.4 per cent per degree.

VIII. PRECISION DISCUSSION

In equation (5) the work done by the expanding gas will be

$$W=\mathrm{B}\Delta v=Bv-Bvi=\frac{m}{M}RT\ (1+\beta_T B)-Bv_i \tag{12}$$

and equation (5) may be written

$$Q=m\left[f(p)+\frac{RT(1+\beta_T B)}{M}\right]-Bv_i \tag{13}$$

in which m is the mass of gas contained in the bomb of volume v_i at the pressure p and temperature T, R is the gas constant, M the molecular weight of the gas, β_T is a small coefficient expressing the deviation from the perfect gas law at atmospheric pressure and T°K, B is the prevailing barometric pressure, and $f(p)$ is the value of ΔU_p^1 for 1 g of the gas at T°K.

Using the value of $\Delta U]_p^1=f(p)$ for air, one can compute the precision required in each measured quantity in order to obtain a desired precision in the quantity ΔU for this gas. If we take $t=25°$ C., $v_i=1$ liter and assume an allowable error of 0.25 cal. from each measured quantity, we obtain the results shown in the following table.

TABLE 1.—*Error in each measured quantity which produces an error of 0.25 cal. in the quantity* $\Delta U]_p^1$

	$\Delta U\,]_{p\ \text{atm.}}^{1\ \text{atm}}$ (air at 25° C.), cal.		22.0	50.0	89.2	139
1	p	atm	20	30	40	50
	δp	do	0.22	0.14	0.11	0.09
2	v_i	l	1	1	1	1
	δv_i	cm ^{3}	10	10	10	10
3	m	g	24	36	48	60
	δm	mg	11	11	11	11
4	B	mm Hg	760	760	760	760
	δB	do	8.2	8.4	8.6	9.1
5	Electrical energy equivalent	cal	485	757	1,048	1,348
	δt	° C.	0.0036	0.0036	0.0036	0.0036
	$\delta t'$	do	.0001	.0001	.0001	.0001
6	Stirring energy	cal	10	10	10	10
	100 δ (S. E.)/ (S. E.)	per cent	2.5	2.5	2.5	2.5
7	T	° K	298	298	298	298
	δT	do	.16	.11	.08	.06
8	β_T	atm.$^{-1}$	.00037	.00037	.00037	.00037
	$\delta\beta_T$	do	.0005	.0003	.0003	.0002

Of the items shown in the table, Nos. 2, 4, 7, and 8 can be eliminated as sources of error since they can obviously be easily measured with much more than the required accuracy.

Item 1.—For the pressure measurements a good calibrated Bourdon gage could be employed for pressures up to 50 atm. At higher pressures a more accurate method of measuring the pressure would be required.[5]

Item 3.—In the mass determination, somewhat more than the required accuracy can be easily obtained with a liter bomb and with a balance sensitive to a few milligrams under loads up to 2 kg.

Item 5.—In determining the electrical energy required to equalize the cooling effect of the expanding gas no significant errors will be made in measuring the actual energy input employed. The total error from this source will be determined by the accuracy of the temperature control during the experiment and the accuracy in determining the small difference between the initial and final equilibrium temperatures. The value of δt shown in the table represents the permissible integrated average temperature difference between the calorimeter and the jacket during the experiment, assuming a reaction time of 10 minutes and an over-all heat-transfer coefficient of 7.2 cal. min.$^{-1}$ ° C.$^{-1}$. The value $\delta t'$ represents the accuracy with which the difference between the initial and final temperatures must be known with a calorimeter having a water equivalent of 2,500 g.

Item 6.—An efficient stirrer will supply energy to the calorimeter at the rate of about 1 cal. per minute. For an allowable error of not more than 0.25 cal. from this source it is obvious that throughout the period of the experiment (30 minutes) the stirring power should be constant within ±2.5 per cent.

From the foregoing discussion it appears that it should be possible without much difficulty, to determine the quantity $\Delta U]_p^1$ for 1 liter of

[5] The necessity of employing a pressure gauge can be dispensed with, if desired, by the use of twin bombs. See Washburn, B. S. Jour. Research, vol. 9, p. 271, 1932.

gas with an error of less than 1 cal. A forthcoming paper by Rossini and Frandsen describes some experimental results obtained by the method.

In conclusion, it may be noted that by combining the calorimetric value for $\left(\frac{\partial U}{\partial p}\right)_T$ with the calorimetric value for μC_p, both $p\left(\frac{\partial v}{\partial p}\right)_T$ and $T\left(\frac{\partial v}{\partial T}\right)_p$ can be directly obtained, if the volume is known, and this is probably the most accurate method of determining these two coefficients.

WASHINGTON, August 3, 1932.

RP488

THE PHOTOGRAPHIC EMULSION; VARIABLES IN SENSITIZATION BY DYES

By B. H. Carroll and Donald Hubbard

ABSTRACT

These experiments were designed to test the effect of independent variables in the emulsion on the relative spectral sensitization by a given dye in a given emulsion. Four typical dyes representing four series were used in combination with emulsions of different types. Relative spectral sensitivity increased slowly with the concentration of dye. In agreement with Sheppard, it was found that the relative spectral sensitivity was little affected by the formation of sensitivity nuclei (from allyl thiocarbamide, for example) which greatly increased the absolute sensitivity to any wave length. Increased alkalinity increased relative spectral sensitivity by an extent which depended on the dye. Increased silver ion concentration generally increases sensitization by any dye, but there are differences between individual dyes which may be explained on the hypothesis that spectral sensitization depends on adsorption of the ion of the dye by the oppositely charged ion of the silver halide lattice; changes in adsorption of basic dyes may be sufficient to counteract the general trend at sufficient excess of silver.

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I. INTRODUCTION

The spectral sensitivity of a given photographic material in either absolute or relative terms is generally recognized to depend both on the dye or dyes, and on the emulsion. The many variables in the emulsion which influence the sensitization by the dye may be divided into those which are characteristic of the particular emulsion, such as the grain size and proportion of iodide, and those which may readily be varied in a given dye-emulsion combination, such as the silver and hydrogen ion concentrations. This paper will be primarily concerned with the latter group of variables. While it is not possible to draw a sharp distinction between these variables and those characteristic of the emulsion and dye, a study of the more general variables of sensitization will make it easier to distinguish characteristics of individual emulsions by comparing them under constant conditions. The process of hypersensitization (1) (2) [1] must obviously be connected with variation of conditions in a given dye-emulsion combination. This will be treated in full in a separate communication; a preliminary report (3) has already been made, using some of the data in this paper.

[1] Numbers in parentheses here and throughout the text refer to the list of references at the end of the paper.

The experimental methods used in this investigation, including emulsion making, sensitometry, and determination of bromide ion concentration, have been described for the most part in previous communications (4) (5). Emulsion formulas followed the types described in one of these references (4) and will be designated by the same letters; full details are available to any interested parties. A measure of the added spectral sensitivity conferred by the dyes was obtained with the sector wheel sensitometer, inserting an appropriate filter between the light source and plate in addition to the Davis-Gibson filter used for correction of the incandescent source to sunlight quality. A Wratten "Minus Blue" (No. 12) filter was most commonly used, as it gives approximately the total sensitivity to all wave lengths longer than those absorbed by the silver bromide; absorption by the filter is not over 15 per cent in the region of sensitization by any of the dyes except pinaflavol. This general method does not determine the relative spectral sensitivity, but it is the most accurate means available for comparison of the sensitization produced by a given dye under varying conditions.

Four dyes were used in the investigation, each representing a different type. Erythrosin, which is the only acid dye in common use as a sensitizer, was included because it was important to have an acid dye for comparison with the basic sensitizers. It is soluble in water in concentrations much higher than those used in emulsions and ionizes into the colorless positively charged sodium ion, and the negatively charged ion of the acid tetraiodofluorescein. The other three dyes are basic, and ionize into colorless iodide or chloride ions, and positively charged ions of the corresponding complex nitrogen bases. They represent three distinct types—pinacyanol is a carbocyanine (6); pinaverdol an isocyanine (6); and pinaflavol, a newer type which has not been assigned a general name (7). The first two are very insoluble in water, being completely extracted from it by solvents such as chloroform, and their suspensions are readily flocculated by electrolytes, especially halides, while pinaflavol does not show these colloidal characteristics and apparently forms true solutions in water at low concentrations. However, even the insoluble dyes may be considered as colloidal electrolytes, as they appear to be highly dissociated; the iodide ion in any of these dyes may be titrated electrometrically with silver nitrate giving values corresponding closely to the calculated molecular weight.

The basic dyes were commercial products, used without further purification; the pinacyanol was the chloride of its base, the others iodides. The erythrosin used in these experiments had been prepared from an old sample of a Kahlbaum product by precipitation of the acid and recrystallization of the sodium salt made from it. It was recently found to be low in iodine, the acid containing 26.5 per cent instead of 60.75 per cent theoretical (8); apparently considerable loss had occurred on storage, with resulting formation of fluorescein. Photographic comparison with a known sample of pure erythrosin received from the color laboratory, Bureau of Chemistry and Soils, showed that it produced its maximum sensitization in exactly the same spectral region as the pure dye, but in about half the proper intensity, and that there was faint sensitization at shorter wave lengths corresponding to that produced by fluorescein. Fortunately

this contamination by the parent acid dye does not affect our conclusions.

The dyes were normally added to the emulsions just before coating, in the form of dilute solutions; the alcoholic stock solutions of the basic dyes were diluted further with water to avoid coagulation of gelatin on contact with the alcohol. In all cases, the dye was added to the liquid emulsion before coating; none of the following experiments deal with sensitization by bathing finished plates.

II. CONCENTRATION OF DYES

The concentration of a given dye in an emulsion is reported to have an optimum value (9), but no quantitative data are available. Eder believed that the sensitivity fell off after passing through the maxi-

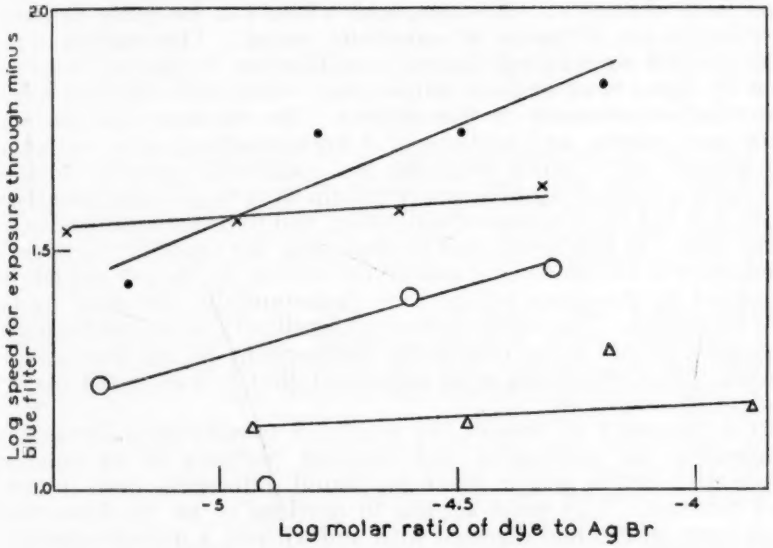

FIGURE 1.—*Effect of concentration of dye on spectral sensitization*

O, Pinacyanol. . Pinaflavol.
X, Pinaverdol. Δ Erythrosin.

mum because of filter action by the dye. With any of the basic sensitizers used in these experiments the upper limit seems to be set rather by the tendency of the dye to cause fog.

The data illustrated in Figure 1 indicate that within the range of concentrations tested, which covers the normal values for these dyes, the sensitization by the dye increases slowly with its concentration. The emulsions used in these experiments were of the neutral (type C, reference (4)) type with 4.0 mol per cent AgI, and were coated at a bromide ion concentration 0.9 to 1.1×10^{-4} and pH 7.1 to 7.3. Speeds were in all cases measured by exposure through the Minus Blue filter.[2] Speed numbers were somewhat dependent on development time, and were, therefore, compared by interpolating the value cor-

[2] Absorption by this filter was not taken into account in calculating the speed numbers, since relative values only were involved.

responding to $\gamma = 1.0$ from plots of speed against γ for each case. The contrast of the emulsions was not appreciably affected by the concentration of dye. The data are plotted on a logarithmic scale for compactness; concentrations have been reduced to the common basis of the molar ratio of dye to silver bromide.[3]

The slopes of the curves for pinaflavol and pinacyanol sensitization are larger than those for the other two dyes. This does not correspond to any classification of dyes; correlation with the adsorption of the dyes on silver bromide may be possible when data are available.

III. AFTER-RIPENING

After-ripening an emulsion, either with the sensitizers naturally occurring in gelatin or with known materials, such as allyl thiocarbamide, can produce a large increase in sensitivity, which is not associated with change in grain size, and which can be quite definitely ascribed to the formation of sensitivity nuclei. The relation of this effect, which we may call nuclear sensitization, to spectral sensitization by dyes, is of obvious importance. Sheppard (10) has briefly described experiments on this subject. An emulsion was made up with inert gelatin, and portions of it were sensitized with erythrosin, pinacyanol and a green sensitizer not specifically named. Another emulsion was made up with active gelatin so as to give the same mean grain size and the same size-distribution, and portions sensitized in the same way. It was found that for each dye, the ratios of red or green sensitivity to the blue-violet sensitivity (that is, for those wave lengths absorbed by the silver halide) were "substantially the same" in the two emulsions. The relative spectral sensitivity of an emulsion was, therefore, found to be practically independent of the formation of nuclei. This conclusion is so important that it was tested under a variety of conditions.

It is necessary to present the results in tabular form, because on comparing the undigested and digested portions of an emulsion made with active gelatin there are found differences both in speed and contrast. The same applies to portions of an emulsion made with inert gelatin and digested with and without a nuclear sensitizer.

Table 1 presents the data for an emulsion made with relatively inert gelatin (prepared by digesting an active gelatin with ammonia and then washing very thoroughly). After washing, the emulsion was divided in halves, to one of which was added a trace of sodium thiosulphate. After digestion, each half was divided into four portions; one was left unsensitized and the other three sensitized with three different dyes. It is impossible to express the resulting differences by single numbers. The contrast was changed both by the thiosulphate and the dyes; of the three dyes, pinacyanol produced much the strongest effect. Furthermore, the relation between speed number and time of development was changed by both types of sensitization. However, we may state with confidence that the increase in sensitivity to the longer wave lengths was less than the increase in total sensitivity (to white light). In this emulsion, the sensitivity to wave lengths transmitted by the Minus Blue filter was a

[3] The molecular weights used for this purpose were: Pinacyanol, 412; pinaverdol, 501; pinaflavol, 366; erythrosin, 898. The concentrations are of the order of a few milligrams of dye per liter of emulsion containing 40 to 45 g of silver bromide.

small fraction of the total, so that white light and blue light sensitivities were equivalent within the necessary limits of accuracy.

TABLE 1.—*Effect of nuclear sensitization, by $Na_2S_2O_3$, on sensitization by dyes*

[Neutral type emulsion, 4 per cent AgI (4–103) coated at pH 6.4, [Br⁻] 9×10^{-5}; half of emulsion sensitized with $Na_2S_2O_3$ sufficient to convert 2 parts AgBr per 100,000 to Ag_2S]

	Dye	Molar ratio dye to AgBr	White light exposure						Minus blue filter exposure						Fog[13]
			Speed			γ			Speed			γ			
			3	6	12	3	6	12	3	6	12	3	6	12	
Control	None	0	35	59		0.26	0.33								0.02
	Pinaflavol	6.7×10^{-5}	40	53	65	.34	.35	0.43	4.0	3.5	3.5	0.26	0.57	0.70	.04
	Erythrosin	1.1×10^{-4}	21.5	46	85	.26	.36	.39	3.5	3.1	3.1	.16	.30	.40	.03
	Pinacyanol	5.9×10^{-5}	31.5	30	25	.55	.77	.95	8.0	7.4	6.3	.76	1.14	1.57	.20
Sensitized with $Na_2S_2O_3$	None	0	430	255	230	.51	.94	1.41							.08
	Pinaflavol	6.7×10^{-5}	315	365	325	.64	.92	1.29	12.3	13.8	13.5	.88	1.07	1.86	.20
	Erythrosin	1.1×10^{-4}	225	235	235	.63	.95	1.40	9.6	9.2	7.6	.57	1.03	1.63	.08
	Pinacyanol	5.9×10^{-5}	120	105	96	.73	1.10	1.66	9.6	9.6	9.1	1.05	1.70	2.42	.41

Similar experiments with other emulsions and two of the dyes are recorded in Table 2. These emulsions had finer grain and lower iodide content, which probably accounts for the much better ratio of red or green sensitivity to blue sensitivity. This ratio was unchanged or somewhat decreased on increasing the total sensitivity by thiocarbamide sensitization.

The emulsions listed in Table 3 were made with active gelatin, and compared with and without digestion after washing. The variation in sensitivity nuclei in this case was obtained by varying the completeness of the reaction with the available sensitizing compounds, instead of by varying the quantity of the latter. The results are very similar to those obtained with the pure sensitizing compounds. The relative sensitivity to longer wave lengths was appreciably decreased by the after-ripening, although the absolute value of sensitivity to red or green increased two or more times.

These last experiments also included the behavior of the dye when present during digestion. Two portions of emulsion were digested under conditions identical except that the dye was added before digestion to one, and after digestion (the usual procedure) to the other. The sensitization by erythrosin was less when it was present during digestion than when it was added afterward (just before coating); pinacyanol was more effective under the former conditions, while pinaflavol was about the same.

TABLE 2.—*Effect of nuclear sensitization, by allyl thiocarbamide, on sensitization by dyes*

[Neutral emulsion (4–48), 1 per cent AgI, coated at pH 7.5, $Br^-1.3\times10^{-5}$; ammonia process emulsion (1–153), 1 per cent AgI, coated at pH 8.3, $Br^-1.3\times10^{-5}$. Half of each emulsion sensitized with allyl thiocarbamide sufficient to convert 8 parts AgBr per million to Ag_2S. "A" red filter used for exposure of pinacyanol sensitized batches; minus blue (yellow) filter for others]

Emulsion	Dye	Allyl thiocarbamide	Blue light exposure ("C" filter)						Yellow or red light exposure						Fog 11
			Speed			γ			Speed			γ			
			3	6	12	3	6	12	3	6	12	3	6	12	
4–48	Erythrosin	Without	14.0	9.5	10.0	0.37	0.61	0.84	7.9	7.9	7.9	0.52	0.74	0.97	0.24
		With	25	25	23	.54	.76	1.12	11.5	11.0	15.2	.60	.86	1.37	.28
	Pinacyanol	Without	11.5	10.0	8.3	.42	.61	.91	15.9	17.4	13.8	.55	.78	1.06	.27
		With	17	12.5	14	.57	.92	1.18	26.3	26.3	25.1	.63	1.07	1.50	.34
1–153	Erythrosin	Without [1]	24.5	24.5	24.5	1.24	1.86	2.21	2.6	2.7	2.8	1.52	2.16	2.36	.23
		With [1]	166	210	235	1.27	1.75	2.12	20.9	20.9	21.9	1.05	1.60	1.90	.29
	Pinacyanol	Without	2.6	2.4	2.6	2.00	2.40	2.75	5.3	5.3	6.4	1.82	2.49	2.73	.28
		With	9.1	9.0	10.5	1.24	1.86	2.23	17.5	17.5	20.0	1.38	2.12	2.58	.63

[1] White light exposures substituted for blue because of low speeds.

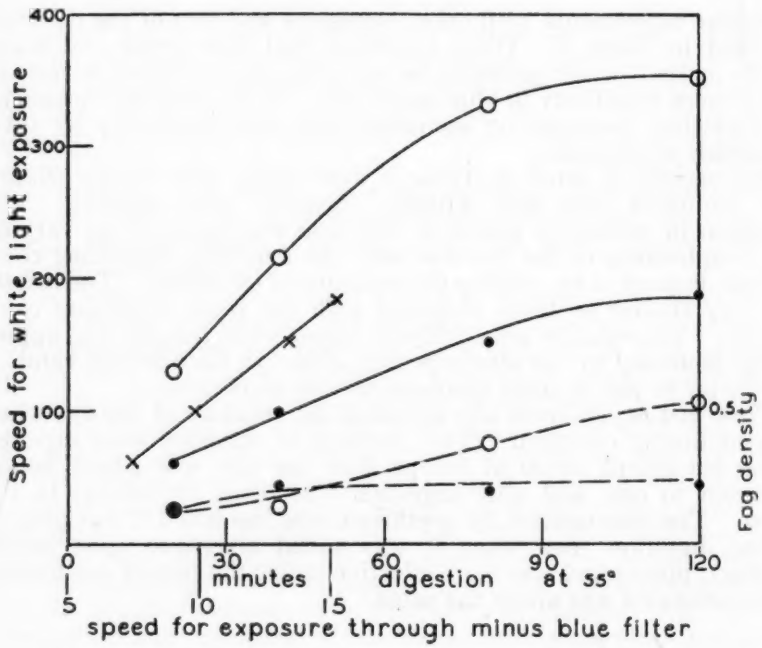

FIGURE 2.—*After-ripening with and without erythrosin in the emulsion*

. With dye. O Without dye.
———— Speed. — — — — Fog.
X Comparison of speed for exposures to white light and through Minus Blue filter at varying stages of digestion.

The data in Table 3 on sensitivities to white light show that the after-ripening was materially retarded by the presence of erythrosin during digestion, while the other two dyes had less effect. Eder (11) observed that some dyes prevented fog when present during ripening.

Lüppo-Cramer (12) has found that in Lippman emulsions erythrosin and other sensitizing dyes can produce a striking retardation of the whole ripening process, and that in normal emulsions erythrosin present during digestion retards after-ripening (13). After-ripening being essentially a surface change in the grains, it is not surprising that it is influenced by the adsorption of a foreign material. Further data were obtained by a slightly different procedure. Emulsions were divided into halves, which were digested at the same temperature and silver ion concentration, one with and one without a sensitizing dye. The results are plotted in Figures 2 and 3 as speeds (at

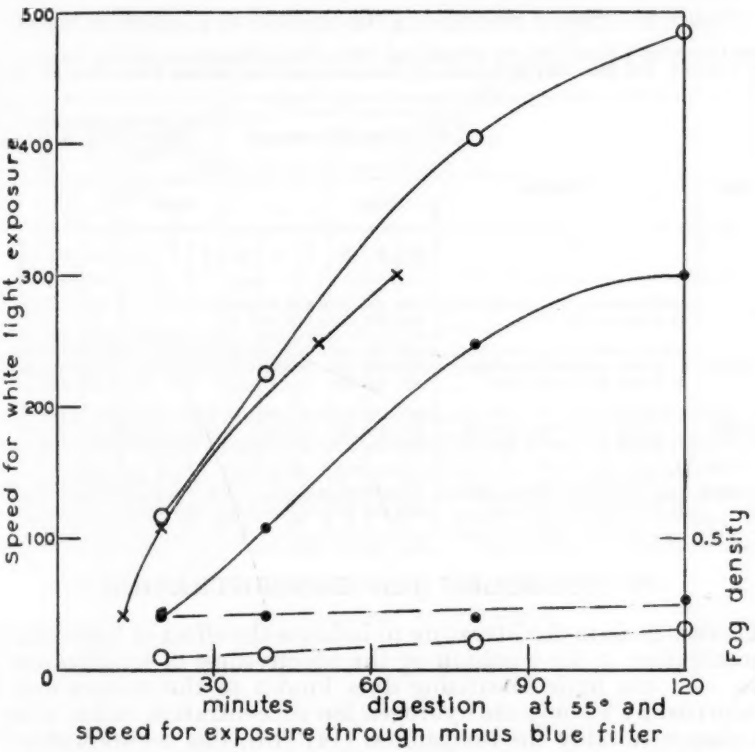

FIGURE 3.—*After-ripening with and without pinacyanol in the emulsion*

. With dye. O Without dye.
——— Speed. — — — — — Fog.
X Comparison of speed for exposures to white light and through Minus Blue filter at varying stages of digestion.

$\gamma = 1.5$) for white light exposures against time of digestion. On the same sheet the speeds (at $\gamma = 1.5$) for exposures through the Minus Blue filter are plotted against the white light speeds. The latter curve would be a straight line if the relative spectral sensitivity were unchanged by the after-ripening.[4] The curvature indicates that it is slightly increased. The other curves show that the rate of after-

[4] In both figures, this curve intercepts the horizontal axis at a small positive value of "speed for exposure through Minus Blue filter," as the speed of the unsensitized emulsion did not fall quite to zero on exposure through the Minus Blue filter.

ripening was divided by about four when erythrosin was present. Pinacyanol approximately halved the rate. Both dyes also retarded the growth of fog. In both figures, the slope of the curve of fog against digestion time is less for the portion digested with dye than for the one digested without it. The effect is less noticeable in Figure 3 because the fog density at any time was increased by the addition of pinacyanol, although the rate of increase with time was less. The data in Table 3 also show that the fog for the portion digested with pinacyanol was less than for the one to which the same amount of dye was added after digestion.

TABLE 3.—*Effect of after-ripening (by digestion) on sensitization by dyes*

[Neutral emulsions 4-50 and 4-51; 2¼ per cent AgI, with subsequent ammonia ripening; coated at pH 5 Br⁻ 1.2×10^{-4}. Red filter used for exposure of pinacyanol sensitized batches; yellow filter for others]

Dye	Digestion	White light exposure						Exposure through yellow (Minus Blue) or red (A) filter						Fog
		Speed			γ			Speed			γ			
		3	6	12	3	6	12	3	6	12	3	6	12	
None	Minimum	50	43	52	0.66	0.94	1.23							0.18
	1.0 hour at 55°	220	302	270	1.01	1.45	2.20							.21
Erythrosin	Minimum	50	40	38	.70	1.02	1.28	3.8	4.0	4.3	0.84	1.17	1.40	.19
	1.0 hour at 55° without dye	265	380	315	.92	1.30	1.85	18	19	22	1.13	1.67	2.28	.30
	1.0 hour at 55° with dye	263	263	240	.78	1.27	1.74	13	13	12	1.20	1.82	2.55	.23
Pinaflavol	Minimum	100	120	115	.67	.85	1.11	6.9	6.6	7.2	1.00	1.40	1.70	.17
	1.0 hour at 55° without dye	138	220	330	.94	1.14	1.71	15.9	15.9	20.0	1.10	1.52	1.97	.79
	1.0 hour at 55° with dye	190	210	288	.86	1.16	1.65	11.5	15.0	16.0	1.17	1.57	2.25	.58
Pinacyanol	Minimum	50	50	57	.65	.88	1.11	6.6	6.6	6.6	.99	1.40	1.69	.33
	1.0 hour at 55° without dye	150	178	175	1.07	1.54	2.37	10.5	9.6	10.5	1.41	2.35	2.91	.58
	1.0 hour at 55° with dye	200	209	220	.97	1.47	2.20	19.0	19.0	15.9	1.00	1.77	2.71	.40

IV. HYDROGEN ION CONCENTRATION

There is little in the literature to indicate the effect of hydrogen ion concentration of the emulsion on the effectiveness of sensitization by dyes. All the basic sensitizing dyes known to the writers may be decolorized by a moderate hydrogen ion concentration and in some of the classes, notably the isocyanines (14) (15), this occurs within the range which might be encountered in emulsions. The sensitizing properties would obviously be expected to diminish with the color. Approximate tests with the dyes used in these experiments showed that pinaverdol is appreciably decolorized by pH less than 7, and is almost completely decolorized by pH 5. Pinacyanol and pinaflavol did not fade appreciably at pH 5.4; the decolorization was barely perceptible at 4.2, and not complete at 2. Erythrosin has an appreciable shift in hue to the yellow, beginning about pH 5.4; the acid is mostly precipitated at pH 3.

The experimental results are presented in Figures 4 and 5, the logarithm of the speed through the Minus Blue filter (at $\gamma=1.5$) being plotted against pH. For comparison, the logarithm of the speed (to white light) of unsensitized portions of the emulsions sensitized with pinacyanol is also plotted in Figure 4. The emulsions were all

digested after washing and before adding the dyes, under the same conditions of temperature, silver ion concentration and pH, and the pH was adjusted just before coating so that it did not affect the after-ripening. With the exception of pinaverdol, the data for each dye (and also for the unsensitized portions) represent two emulsions, one for the range below pH 7 and one for the range above. These fit

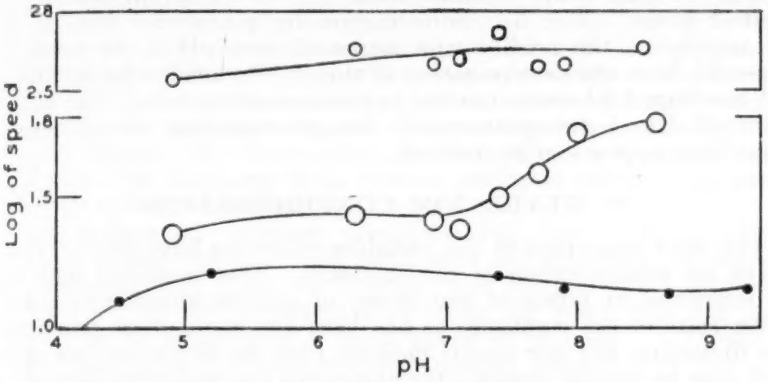

FIGURE 4.—*Variation in sensitivity with hydrogen ion concentration*

o Speed for white light exposure, unsensitized emulsions.
O Speed for exposure through Minus Blue filter, pinacyanol-sensitized emulsions.
. Speed for exposure through Minus Blue filter, pinaverdol-sensitized emulsion.

sufficiently well to draw single curves, except for erythrosin. (Fig. 5.) The discrepancy between the two emulsions in this case is explained by a difference in silver ion concentration, to which erythrosin is especially sensitive. The emulsion used for the acid range had a silver ion concentration at pH 7 of 1.3×10^{-8}, while the concentration for the other was 0.66×10^{-8} at the same pH. The effect of differences in

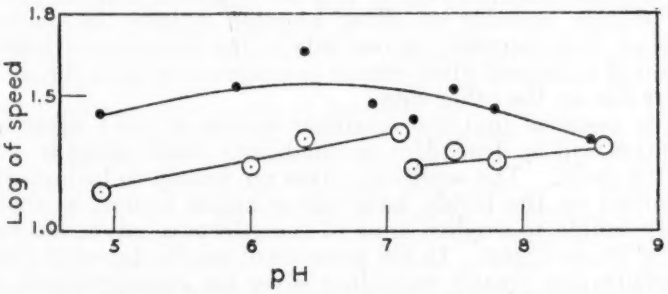

FIGURE 5.—*Variation in sensitivity with hydrogen ion concentration*

All exposures through Minus Blue filter.
. Pinaflavol-sensitized emulsions.
o Erythrosin-sensitized emulsions.

silver ion concentration in other cases was negligible. These emulsions were made with a gelatin giving very little change in sensitivity of the unsensitized emulsions with pH (upper curve in fig. 4), so so that this complication was reduced to a minimum.

The effect of hydrogen ion concentration on sensitization by the dyes was apparently characteristic of the individual dye. At the

most, it was less than the effect of silver ion concentration, as may be seen by comparison with the curves of Figures 6, 7, 8, and 9, which are on the same scale. Pinacyanol in the alkaline range (fig. 4) showed the largest effect, with little change between pH 7 and 5. Erythrosin consistently increased in effectiveness with increasing pH; this may possibly be explained by increasing dissociation, as it is the salt of a weak acid. Pinaflavol showed a maximum around the neutral point. (Fig. 5.) Sensitization by pinaverdol (fig. 4), fell off rapidly as the acidity was increased past pH 5, as would be expected from the decolorization of this dye by acid. Sensitivity at pH less than 4.5 became too low to measure accurately. The change from pH 5 to 9 was quite small. No generalization on the basis of these data appears to be justified.

V. SILVER ION CONCENTRATION

The most important of the variables which we have studied is the silver ion concentration of the emulsion. This condition may also be expressed in terms of the excess of soluble bromide or soluble silver salts in the emulsion, as has been the commonest practice in the literature, but our results indicate that the silver ion concentration may be used to simplify the statement and understanding of the condition in a manner quite analogous to the use of hydrogen ion concentration for acidity and alkalinity. As explained in previous communications (4) (5), the emulsion may be considered as saturated with silver bromide, so that the product of silver and bromide ion concentrations is a constant at a given temperature (9×10^{-13} at 30°) and either concentration may be computed from the potential of a silver electrode in the emulsion and used to express its condition. The addition of soluble bromide to an emulsion thus decreases its silver ion concentration; the addition of a soluble silver salt increases the silver ion concentration. In both cases the rate of change is less in the emulsion than it would be in plain aqueous solution. Adsorption of soluble bromide on silver bromide retards the increase in bromide ion concentration on one side of the equivalence point, and formation of unionized silver-gelatin compounds reduces the silver ion concentration on the other side.

As it is essential that the sensitizer should dye the silver halide, sensitization will be dependent on conditions which affect its adsorption to the grain. The sensitizing dyes are known to be ionized, and are adsorbed on the highly polar silver halide lattice, so that it is relatively simple to predict some of the effects of silver ion concentration in the emulsion. In the presence of soluble bromide (bromide ion concentration greatly exceeding silver ion concentration), silver bromide will strongly adsorb bromide ions at the silver ions of the crystal lattice, and will acquire a negative charge. The adsorption of the negatively charged ion of an acid dye, such as erythrosin, will thus be reduced, since it must compete with the bromide ions for the silver ions of the lattice. The presence of an excess of silver will, conversely, increase the adsorption of the color ion of an acid dye on silver bromide, because the silver ions of the lattice will be free of adsorbed bromide and thus more available to the ions of the dye.[5]

[5] It should be remembered that in a gelatin emulsion, the adsorption of the gelatin to the silver bromide interferes very materially with the adsorption of either type of dye. This is almost certainly one of the reasons why gelatin emulsions are not sensitized as readily as collodion emulsions.

By the same type of reasoning we may predict that the adsorption of basic dyes should be greater in the presence of an excess of bromide ions, and should be reduced by an excess of silver ions.

The shift in adsorption of dyes with silver ion concentration is used in the titration of silver against halogen with adsorption indicators (16). It is of interest that the best results are obtained with acid dyes (fluorescein and the eosins, including erythrosin) and that the basic dyes which can be used as indicators (17), methyl violet for example, may be used as sensitizers for collodion emulsions. The first observation of the effect was apparently made by von Hübl (18) who discovered a change in color of cyanine on silver bromide with the addition of excess silver or bromide to the solution. Lüppo-Cramer (19) found that, in accordance with the theory, erythrosin was displaced from various insoluble salts by the corresponding anions, while basic dyes were not.

Observations on collodion emulsions (20) have been in accord with the simple theory. Acid sensitizers are adversely affected by the slightest traces of soluble bromide, and are preferably used with the addition of soluble silver salts, while the basic dyes are most effective in the presence of a slight excess of bromide. It should be remembered that collodion emulsions are not sensitized by the basic dyes, such as pinacyanol, until the alcohol has been largely displaced by washing with water, so that we are justified in discussing the ionization on the basis of an aqueous system.

Lüppo-Cramer (21) (22) found that in sensitizing gelatin emulsions by bathing, erythrosin was more affected by soluble bromide in the dye bath than was the basic dye pinachrome. However, the simple theory just given fails to predict that small amounts of soluble bromide will cause any decrease in sensitization by basic dyes, and something further is necessary to account for the fact that this decrease exists and is of such magnitude that most writers have failed to note the difference between the behavior of the acid and basic dyes. In the first place, the adsorption of the basic sensitizing dyes on silver bromide is not as simple as that of erythrosin. Sheppard, Lambert, and Keenan (14) found that at pH 5, pinacyanol was adsorbed much more strongly on silver bromide with excess of silver ions than on the same sample with excess of bromide ions. At pH 7.5 the order was reversed. Adsorption of dichlorofluorescein followed the simple theory. Bokinik (23) also reports stronger adsorption of pinacyanol on silver bromide with excess of silver ions than on an "equivalent" sample; the pH is not given. More data on adsorption of the basic sensitizers is evidently necessary for adequate theoretical treatment. In the second place, there is the possibility of some factor depending on silver ion concentration and affecting acid and basic dyes alike, the effects of changes in adsorption being superposed on this. In a system such as the photographic emulsion where gain or loss of bromine is probably the significant chemical change, the oxidation-reduction potential should depend on the silver (or bromide) ion concentration in a manner exactly analogous to its dependence on hydrogen ion concentration. If we adopt the working hypothesis that sensitization is the result of chemical reduction of silver bromide by the dye, a decrease in sensitization by increasing bromide ion concentration is to be expected. This hypothesis involves the simplest and most definite mechanism of sensitization, and in the absence of

proof to the contrary,[6] we believe it is worthy of support (24). It is essentially the converse of the oxidation theory of desensitization. The implied continuous gradation between sensitization and desensitization has been realized by Kögel and Bene (27) and in this laboratory (28) by change in silver ion concentration. Independent evidence of photochemical reaction between silver bromide and sensitizing dyes is given by the accelerated bleaching of the dyes when adsorbed on silver bromide.

As the relative magnitude of the effects of changes in oxidation-reduction potential and in adsorption can not be predicted, the change in sensitization with silver ion concentration, which is the algebraic sum of these effects, may take a variety of forms, but we may at least expect that the basic dyes will be less sensitive to the addition of soluble bromide than the acid dye.

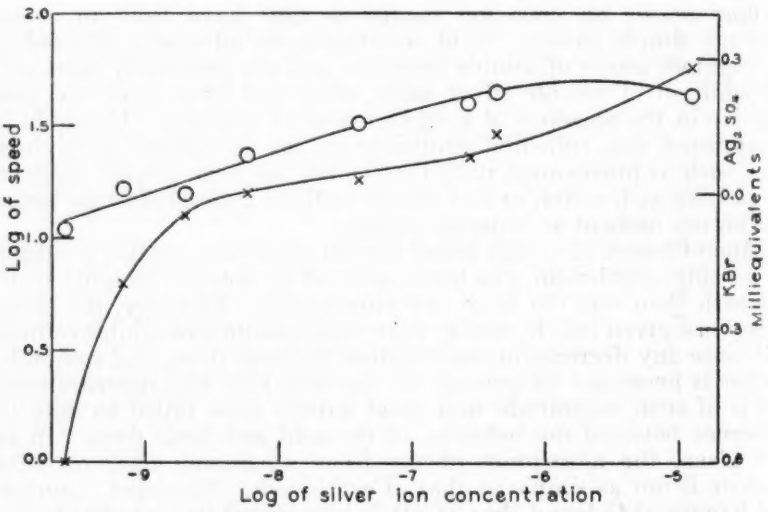

FIGURE 6.—*Variation in sensitivity with silver ion concentration*

O Speed of pinaverdol-sensitized emulsion for exposures through Minus Blue filter.
X Quantities of silver sulphate or potassium bromide added to 175 ml of emulsion, containing 0.040 equivalent of silver bromide, to produce indicated silver ion concentrations.

Our data are presented in Figures 6, 7, 8, and 9. The logarithm of the speed (at $\gamma = 1.0$) for exposures through the Minus Blue filter has been plotted against the logarithm of the silver ion concentration in the emulsions. The logarithmic scale for the speed numbers was adopted as the best means of comparing the data for emulsions which differed considerably in speed. The total (white light) sensitivity of

[6] The results of Leszynski (25) have been widely quoted as proof that sensitization can not depend on photochemical reaction between the dye and the silver halide, since it is practically impossible thus to account for his reported yield of 20 atoms of photo-silver per molecule of erythrosin (without development). The writers are, however, unable to accept his data as adequate to a crucial test. The figure just quoted was obtained by ascribing to the action of the sensitizer all the silver found in an erythrosin-sensitized emulsion after exposure to green light, but Leszynski's own data show that the exposure used to secure the above yield was 10^8 times that necessary to produce a developable density of 1 in the same emulsion without the erythrosin, using exactly the same source of green light (an incandescent light with filter). Granting that green light was many times more effective in producing a developable image in the erythrosin-sensitized portion of the emulsion than in the unsensitized, the absence of control analysis on the unsensitized emulsion after the same exposure renders his conclusion very uncertain, especially as no details are given for his experiments which lead him to believe that the Becquerel effect was not involved. The results of Tollert (26) are open to the same criticism for lack of control experiments.

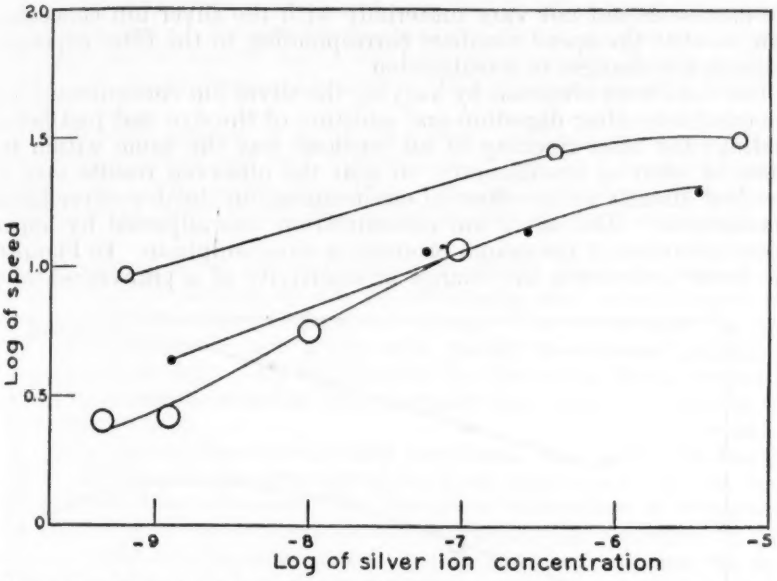

FIGURE 7.—*Variation in sensitivity with silver ion concentration, for erythrosin-sensitized emulsions*

., o Neutral emulsions.
O Ammonia-process emulsion.
All speeds for exposures through Minus Blue filter.

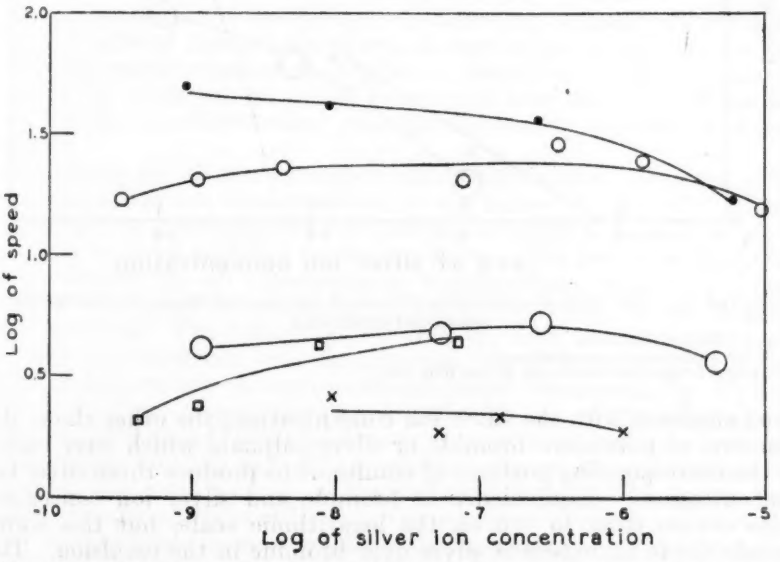

FIGURE 8.—*Variation in sensitivity with silver ion concentration, for pinaflavol sensitized emulsions*

., o Neutral emulsions.
X, □ Ammonia-process emulsions.
All speeds for exposures through Minus Blue filter.

the emulsions did not vary materially with the silver ion concentration, so that the speed numbers corresponding to the filter exposures indicate the changes in sensitization.

The data were obtained by varying the silver ion concentrations of the emulsions after digestion and addition of the dye and just before coating; the after-ripening of all portions was the same within the limits of error of sensitometry, so that the observed results may be ascribed directly to the effect of environment on the dye-silver halide combination. The silver ion concentration was adjusted by appropriate additions of potassium bromide or silver sulphate. In Figure 6, one curve represents the change in sensitivity of a pinaverdol-sensi-

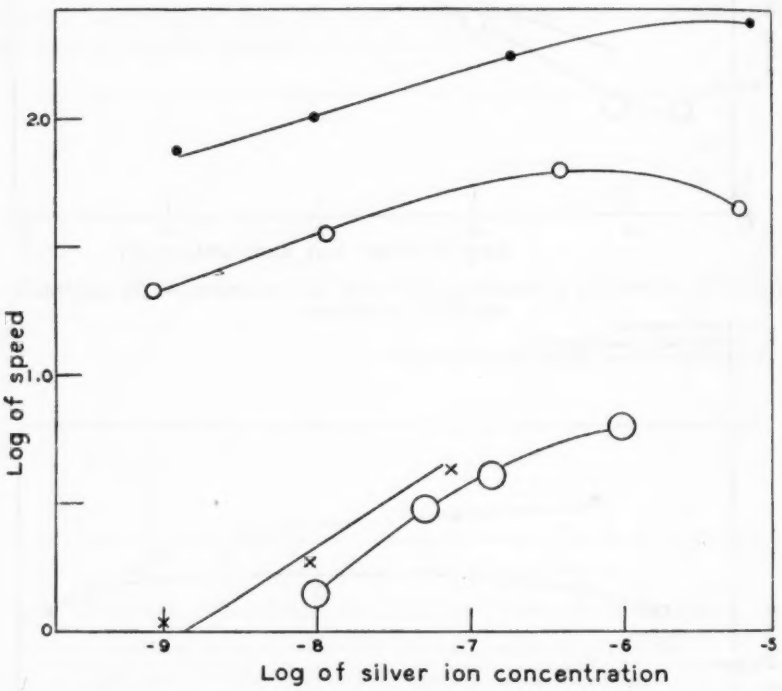

FIGURE 9.—*Variation in sensitivity with silver ion concentration, for pinacyanol-sensitized emulsions*

•, ○, Neutral emulsions.
X, Ò Ammonia-process emulsions.
All speeds for exposures through Minus Blue filter.

tized emulsion with the silver ion concentration; the other shows the amounts of potassium bromide or silver sulphate which were added to the corresponding portions of emulsions to produce these silver ion concentrations. Equivalence of bromide and silver ion concentrations occurs close to -6 on the logarithmic scale, but this corresponds (5) to an excess of silver over bromine in the emulsion. The emulsion after washing (with no addition of bromide or silver) contained only a very slight amount of soluble bromide, but the silver ion concentration was repressed by the gelatin, and, therefore, was much smaller than the bromide ion concentration. The curve obviously corresponds to the change in potential of a silver electrode on passing

through the equivalence point of a titration of silver against bromide; in the presence of the gelatin at this pH (about 7), the equivalence point is displaced toward increasing bromide ion concentration and the "break" is not as sharp. The results with other emulsions were very similar.

Two general classes of emulsions were used—the neutral ("C") type, with 4.0 mol per cent AgI, coated at pH 7 ± 0.5, and the ammonia ("A") type, with 1.0 mol per cent AgI, coated at pH 8 to 8.5. No differences which could be ascribed to the emulsion type were detected.

The range of silver ion concentrations which could be used in the experiments was limited by the increasing fog and instability of the batches with increasing excess of silver. The emulsions for this series of experiments were made with partly deactivated gelatin in order to reduce fog. The fog density for 12-minute development in pyro-soda without bromide was normally less than 0.5, and in no case exceeded 0.75.

By centrifuging the experimental emulsions, they could be cleared of silver halide and the concentration of any dye which had not been adsorbed could be observed. The change in adsorption of erythrosin with changing silver ion concentration was readily detected in this way. It could not be measured with any accuracy because the dye changed in hue as well as in concentration, but by comparison with known solutions of the dye made up in a gelatin solution corresponding to the emulsion, it was estimated that in one emulsion, half the dye was adsorbed at a silver ion concentration of 1.2×10^{-9}, while five-sixths was adsorbed at a silver ion concentration of 3×10^{-6}. Pinacyanol and pinaverdol in photographically practicable concentrations were adsorbed too strongly to make any comparison possible, while the color of the gelatin, plus a change in hue of the dye, interfered with measurements of pinaflavol remaining in the emulsion. Quantitative work will obviously have to be done under other conditions, but it is worth recording that the effect could be detected in the emulsion.

The curves for all the dyes show that sensitization decreases with decreasing silver ion concentration in the range 10^{-7} to 10^{-10} which corresponds to concentrations of soluble bromide sufficient to give moderate to good stability to the emulsion. This indicates that the effect common to all dye-emulsion combinations, which we have ascribed to change in oxidation-reduction potential, is the largest factor involved. The differences between the dyes are significant and generally in accordance with the expected change in adsorption. The slopes of the curves for erythrosin-sensitized emulsions (fig. 7) are larger than those of emulsions sensitized with any of the other dyes, since the adsorption of this acid dye increases with increasing silver ion concentration and the sign of the resulting change in sensitization is, therefore, the same as that of the common factor. The curves for sensitization by all three of the basic dyes appear to reach a maximum value, the decrease in sensitization with increasing silver ion concentration being most certainly established for pinaflavol (fig. 8) and least certainly for pinacyanol. (Fig. 9.) The slopes of the curves on the bromide side of the maximum are least for pinaflavol and greatest for pinacyanol, pinaverdol being intermediate. Pinaflavol is by far the most soluble of the three basic dyes, and observations under com-

parable conditions both in the emulsion and with pure silver bromide indicate that it is less completely adsorbed than the other two. Changes in adsorption caused by change in silver ion concentration should, therefore, have more effect on the sensitization by pinaflavol than on that by the other basic dyes, and it is to be expected that the general trend should be more completely counteracted by the predicted decrease in adsorption with increasing silver ion concentration. The net result is that the change in sensitization by pinaflavol is close to the experimental error over a considerable range of silver ion concentration, although there is an unmistakable decrease at a sufficient excess of silver.

Increase in relative spectral sensitivity by increasing the silver ion concentration in the emulsion is very seriously limited in practice by the instability of the resulting product. If the emulsion must be kept for 6 to 12 months under ordinary conditions without serious deterioration (which might be regarded as the minimum commercial requirement) it is necessary in emulsions of the type used in these experiments to have the silver ion concentration approximately 2×10^{-9} N or less. (This corresponds to 2 to 3 molecules of soluble bromide per 1,000 of silver bromide). Silver ion concentrations up to 10^{-5} N are produced in hypersensitized materials (3), but these correspond to a useful life of a few weeks or even days. Deterioration of the emulsions in which the silver ion concentration was adjusted before coating went on at a rate increasing with this factor; the batches with the highest concentrations indicated behaved like hypersensitized materials.

A number of patents (29) have recently been secured on organic materials which are described as preservatives for emulsions. One of these, nitrobenzimidazol, has also been studied (30) as a substitute for soluble bromide in development. Since its use is patented, any practical investigation by this laboratory is unjustified, but the mechanism of its action is of considerable scientific interest. Nitrobenzimidazol was synthesized in this laboratory and purified by recrystallization from hot water and from alcohol. Its crystals formed the characteristic groups of flesh-colored needles, and melted at 209° C. The silver compound was prepared by precipitation from dilute aqueous solutions of nitrobenzimidazol and silver nitrate. After thorough washing, the silver ion concentration in saturated solutions of the compound was determined by the silver electrode at 30° C. At pH 7.1 (in 0.010 N sodium acetate solution) it was found to be 2.3×10^{-7} N, indicating that the compound is more insoluble than silver bromide. The silver is, however, readily displaced by hydrogen, since at pH 3.5 (0.010 N acetic acid) the silver ion concentration in a saturated solution was 6.4×10^{-5} N. In emulsions at approximate neutrality it produces some decrease in silver ion concentration, but experiments on afterripening with the addition of nitrobenzimidazol indicated that mol for mol, it produces about ten times the effect of soluble bromide in delaying afterripening. Something more than the decrease in silver ion concentration must be involved, and another method of attack would be necessary to decide what this might be.

Experimental emulsions were divided after digestion into portions which were, respectively, coated unsensitized and sensitized with erythrosin, pinaflavol, and pinacyanol, each of these being subdivided

nto halves with and without the addition of nitrobenzimidazol. It was found that the preservative selectively depressed the sensitivity conferred by the dyes, the effect being greater for the exposures through the filter than for the white-light exposures of the unsensitized portions. The effect was of the same order of magnitude as would be produced by soluble bromide with the same preservative action, although our data do not exclude the possibility that under other conditions this stabilizer might be superior to soluble bromide in this respect. The effect of the nitrobenzimidazol on the individual dyes was appreciably different from that of soluble bromide. The depression of sensitization increased in the order erythrosin < pinaflavol < pinacyanol. A possible explanation may again be found in terms of adsorption. The insolubility of the silver compound of nitrobenzimidazol indicates that this material should be strongly adsorbed by the silver bromide, most probably by the silver ions. This would bring it into competition with the basic, rather than the acid dyes, so that erythrosin should be the least affected of the three.

VI. Acknowledgment

C. M. Kretchman has rendered valuable assistance in coating and testing the experimental emulsions.

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A METHOD FOR THE SEPARATION OF RHODIUM FROM IRIDIUM AND THE GRAVIMETRIC DETERMINATION OF THESE METALS

By Raleigh Gilchrist

ABSTRACT

A method is described for the analytical separation of rhodium from iridium by means of titanous chloride. Two precipitations of the rhodium, as metal, from a solution of its sulphate in sulphuric acid were found to be sufficient to separate it completely from iridium. Following the separation, methods are described for the determination of rhodium by precipitation with hydrogen sulphide, for the elimination of titanium by precipitation with cupferron, and for the determination of iridium by hydrolytic precipitation.

An alternative method is offered in which rhodium and iridium are determined together in one sample by hydrolytic precipitation, and rhodium separately in a second sample.

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I. INTRODUCTION

The separation of rhodium from iridium has long remained one of the most difficult of the analytical problems of the platinum group of metals. Berzelius,[1] in a general scheme for the analysis of crude platinum, used molten potassium bisulphate to separate these two metals from one another. This method is unsatisfactory because of the incomplete removal of rhodium and the partial solution of iridium.

Another method, which is in current use, was employed by Claus,[2] and by Leidié [3] in schemes for the analysis of crude platinum. In these schemes the separation is based upon the precipitation of quadrivalent iridium as ammonium chloroiridate by ammonium chloride. Experience in this laboratory with the purification of the platinum metals has shown that rhodium contaminates iridium, when the latter is precipitated as ammonium chloroiridate, and that it can be eliminated only with great difficulty, if at all, by repeated precipitation of the iridium. Furthermore, since ammonium chloroiridate has a slight solubility, some of the iridium must remain with the rhodium.

[1] J. J. Berzelius, Ann. Physik (Pogg.), vol. 13, p. 533, 1828.
[2] C. Claus, Beiträge zur Chemie der Platinmetalle, Dorpat, 1855, p. 55.
[3] E. Leidié, Compt. rend., vol. 131, p. 188, 1900.

In a recent article, Ogburn and Miller [4] proposed a method for the determination of osmium in which strychnine sulphate, $C_{21}H_{22}O_2N_2 - H_2SO_4$, is used as a precipitating reagent. Attempts were made to determine whether this reagent could be used to effect the separation of iridium from rhodium. The reactions of strychnine sulphate with solutions of the quadrivalent platinum metal chlorides were observed. In each case a precipitate was obtained. No precipitate was obtained in chloride solutions of tervalent rhodium, tervalent iridium, or tervalent ruthenium (quadrivalent ruthenium chloride which had been heated with alcohol). In its reaction with the quadrivalent chlorides, the strychnine salt appears to behave like an ammonium salt, but with the production of compounds of much lower solubility.

It was found possible to precipitate iridium completely from solutions of ammonium chloroiridate in diluted hydrochloric acid (5 + 95).[5] The reagent, moreover, caused no precipitation of rhodium from similarly acidified solutions of pure rhodium chloride. However, when strychnine sulphate was added to solutions containing both iridium and rhodium as chlorides, the iridium was found to be contaminated by rhodium to the extent of from 10 to 37 per cent of the rhodium present in the solutions. It was found possible to redissolve the iridium precipitate by treatment with nitric acid or with sodium nitrite, but it was not found possible to treat the solution in such a way as to permit the quantitative reprecipitation of the compound.

Wada and Nakazono,[6] while studying the behavior of titanous sulphate toward various elements, observed that this reagent caused complete precipitation of metallic rhodium from solutions of its chloride, whereas iridium was not precipitated from its chloride solution. Apparently, the effect of the reagent on solutions containing both rhodium and iridium was not studied.

Attempts, in this laboratory,[7] to use the foregoing reactions as a method of separation showed that the precipitated rhodium was contaminated with as much as 10 per cent of the iridium present. In the absence of any known means of redissolving the precipitate and thus preparing it for a second precipitation, the best that could be done was to fuse the ignited metal with pyrosulphate, in order to extract the rhodium. It was found that a small amount of iridium passed into solution and that the residues from the pyrosulphate fusions always retained some rhodium. The method, therefore, could not be made strictly quantitative but, in spite of its shortcomings, it was better than any other known procedure. The objects of the work described in this paper were to develop this method of separation into a strictly quantitative one and to provide suitable methods for the determinations of the two metals after they had been separated.

II. COMPOUNDS USED IN THE EXPERIMENTS

The iridium and the rhodium which were used throughout the investigation were purified by methods previously described [8] and were found to be free from impurities by spectrographic analysis.

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[4] S. C. Ogburn, jr., and L. F. Miller, J. Am. Chem. Soc., vol. 52, p. 42, 1930.

[5] This denotes 5 volumes of hydrochloric acid, specific gravity, 1.18, mixed with 95 volumes of water. This system of designating diluted acids is used throughout this paper. If no dilution is specified, the concentrated reagent is intended. The concentrated sulphuric acid used had a specific gravity of 1.84.

[6] I. Wada and T. Nakazono, Sci. papers Inst. Phys. Chem. Research, Japan, vol. 1, p. 139, 1923.

[7] Unpublished work by W. H. Swanger and by H. A. Buchheit.

[8] E. Wichers, R. Gilchrist, and W. H. Swanger, Trans. Am. Inst. Mining Met. Eng., vol. 76, p. 602, 1928.

In order to avoid errors incident to volumetric measurements, weighed portions of the compounds, ammonium chloroiridate and ammonium chlororhodite, were used. Care was taken to avoid the presence of alkali chloride or of other nonvolatile impurities in the salts, but no attempt was made to prepare compounds of definite composition. The salts were carefully mixed by grinding in an agate mortar and the metallic content determined by direct ignition in hydrogen whenever a series of samples was weighed. It was never calculated from the theoretical composition of the salt.

III. DETERMINATION OF IRIDIUM BY HYDROLYTIC PRECIPITATION

By far the most difficult phase of the problem under consideration was that which dealt with the determination of the iridium after its separation from rhodium by tervalent titanium. Since the solution at this stage contains the titanium which has been added, it is necessary to effect a separation of the iridium from titanium. The most direct way to do this is to precipitate the iridium by hydrogen sulphide.[9] Certain difficulties were encountered in an attempt to use hydrogen sulphide, such as incomplete precipitation of iridium and partial hydrolysis of titanium compounds, even though considerable quantities of tartaric acid were added to the solutions. The deposition of titanium dioxide was particularly noticeable on the walls of the beaker just above the level of the solutions. The titanium dioxide often formed an adherent mirror on the glassware. It likewise contaminated the sulphide precipitate and could be removed later only by fusion with bisulphate. The recovery of iridium by hydrogen sulphide will undoubtedly have many advantages when the proper conditions of control have been fully established. For the present, however, it seemed expedient to consider some other means by which the iridium could be recovered.

Preliminary experiments showed that the titanium could be entirely eliminated by precipitation with cupferron (ammonium salt of nitrosophenylhydroxylamine, $C_6H_5N{\cdot}NO{\cdot}ONH_4$). It was found that the small quantity of iridium, of the order of 1 mg or less, which contaminated the first cupferron precipitate, was completely recovered by reprecipitating the titanium.

Previous work on the determination of ruthenium [10] and of osmium [11] by hydrolytic precipitation suggested that a similar method was feasible for iridium. Sodium bicarbonate was added to boiling aqueous solutions of ammonium chloroiridate until the color became green. Sodium bromate was then added and the solutions were boiled for 25 minutes to coagulate the finely divided precipitate and to insure complete precipitation. The greenish-black precipitates were treated as described in the procedure given later. The acidities of the filtrates from the hydrolytic precipitation were determined approximately by means of indicator solutions. In four of the solutions from which complete recovery of the iridium was obtained, the acidities ranged from pH 4 to pH 4.6. In the fifth filtrate the pH

[9] This method of recovery of iridium has certain advantages which make it of importance in the analytical chemistry of the platinum group. While the exact conditions which will allow complete precipitation of iridium have not yet been fully established, further work is being done and will appear later in the description of a general method for the separation of the platinum group.

[10] Gilchrist, B. S. Jour. Research, vol. 3, p. 993, 1929.

[11] Gilchrist, B. S. Jour. Research, vol. 6, p. 421, 1931.

value was somewhere between 1.5 and 4. This filtrate was found to contain a small quantity of iridium.

In order to establish proper conditions for the iridium precipitation, it became necessary to be able to detect small amounts of iridium in the filtrates from the hydrolytic precipitations. A test which has been frequently employed in this laboratory consists in the development of a green or blue color [12] when a concentrated solution of sulphuric acid, containing iridium, is heated with nitric acid. With quantities of iridium less than 0.1 mg, the color developed is green, with larger amounts it is blue. A few precautions, however, must be observed. Chlorides appear to decompose the particular compound responsible for the blue color. The sulphuric acid, therefore, must be heated until heavy vapors are evolved and this treatment repeated, after the addition of a small quantity of nitric acid, until all hydrochloric acid is expelled. Furthermore, the strongly acid solution must not be heated for too long a time after the last addition of nitric acid. If these two precautions are observed, the color will often remain visible for as long as a week. The test is likewise applicable when considerable quantities of alkali sulphates are present. If the composition of the evaporated solution be made to approximate that of sodium bisulphate, with a slight excess of sulphuric acid, the color of the salt on solidification will often remain visible for several weeks, changing slowly from blue to violet with the absorption of water from the air. The limiting quantity of iridium capable of certain detection, under the conditions mentioned above, appeared to be 0.1 mg.

The results of the determination of iridium by hydrolytic precipitation from aqueous solutions of ammonium chloroiridate are given in Table 1. The error in No. 12 is ascribed to the fact that the solution was too acid.

TABLE 1.—*Recovery of iridium from aqueous solutions of ammonium chloroiridate by hydrolytic precipitation*

No	$(NH_4)_2IrCl_6$ taken 42.69 per cent Ir	Iridium present	Iridium recovered	Error	pH of filtrate	H_2SO_4-HNO_3 test of filtrate
	g	*g*	*g*	*g*		
10	0.1850	0.0790	0.0790	0.0000	[1] 4	Very faint. Greenish color.
12	.2210	.0943	.0931	−.0012	1.5–4	Deep blue.
13	.2602	.1111	.1112	+.0001	4.3–4.5	Colorless.
14	.3121	.1332	.1332	.0000	[1] 4	Do.
15	.1869	.0798	.0798	.0000	[1] 4.6	Do.

[1] Approximately.

Since the solution from which the iridium must be recovered after the elimination of titanium will contain a considerable quantity of sulphuric acid, it was necessary to establish the conditions for precipitating iridium from such a solution. Solutions of iridium in 10 ml of sulphuric acid were prepared according to directions given later in the section on recommended procedure. These solutions were diluted with 20 ml of water and 10 ml of hydrochloric acid and boiled for 15 minutes. The solutions were then further diluted, filtered, and

[12] Fresenius, T. W., Qualitative Chemical Analysis (John Wiley & Sons, New York, N. Y.), English translation of 17th German ed. by C. Ainsworth Mitchell, 1921, p. 377.

almost neutralized with a solution of sodium bicarbonate. A considerable quantity of sodium bicarbonate was required (approximately 30 g), but this caused no difficulty in the precipitation. The desired end point (pH 4), in the addition of the sodium bicarbonate solution, was indicated by the appearance of a blue color when a drop of brom phenol blue solution (0.04 per cent) was allowed to run down the stirring rod to which clung a drop of the boiling solution. The presence of bromate made the above manner of testing the only one feasible. The solutions were boiled for 25 minutes and filtered. The precipitates were treated as directed in the section on recommended procedure.

The results of the determination of iridium by hydrolytic precipitation at pH 4 from solutions strongly acid with sulphuric acid and hydrochloric acid are given in Table 2. The incomplete precipitation in Nos. 56 and 57 is ascribed to the fact that the desired end point was not quite reached.

TABLE 2.—*Recovery of iridium from solutions of iridium sulphate in sulphuric acid by hydrolytic precipitation*

No.	$(NH_4)_2IrCl_6$ taken 42.70 per cent Ir	Iridium present	Iridium recovered	Error	H_2SO_4-HNO_3 test of filtrate
	g	*g*	*g*	*g*	
56	0.4139	0.1767	0.1762	−0.0005	Faint bluish color.
57	.3297	.1408	.1403	−.0005	Do.
58	.4029	.1720	.1721	+.0001	No iridium detected.
24	.3510	.1499	.1501	+.0002	Faint greenish color, not more than 0.2 mg Ir.
28	.3410	.1456	.1457	+.0001	Very faint greenish color, not more than 0.1 mg Ir.
32	.4128	.1763	.1764	+.0001	Do.

While it was found that iridium was completely precipitated from solution by hydrolysis at pH 4 in the presence of bromate, it was desirable to learn whether the precipitation was quantitative over a range of pH values and whether the addition of bromate was essential. It was found that precipitation at pH 6 was quantitative and that a shorter time of boiling, 10 minutes, was sufficient, provided bromate was present. Solutions of iridium which had been merely saturated with chlorine failed to yield complete precipitation. Solutions of iridium, which had been evaporated with nitric acid and subsequently with hydrochloric acid, turned green at pH 6 and did not yield complete precipitation without the addition of bromate. In connection with this last-named treatment, it was found that the previous addition of nitric acid did not prevent the precipitation of iridium as it does in the case of ruthenium.[13]

IV. METHOD RECOMMENDED FOR THE SEPARATION OF RHODIUM FROM IRIDIUM AND FOR THE DETERMINATION OF THESE METALS

1. PREPARATION OF THE SOLUTION

Place the solution containing the rhodium and iridium as chlorides in a 500 ml Erlenmeyer flask, closed with a short-stemmed funnel. Add 10 ml of sulphuric acid and 2 to 3 ml of nitric acid and evaporate

[13] See footnote 10, p. 549.

until heavy vapors of sulphuric acid are evolved. Add several portions of nitric acid from time to time and continue to heat over a free flame, keeping the solution in constant motion. Dilute the cooled solution with 20 ml of water and again evaporate until vapors of sulphuric acid appear. This is done to destroy nitroso compounds which may interfere in the precipitation of rhodium by titanous chloride.

2. SEPARATION AND DETERMINATION OF RHODIUM

Transfer the solution to a clean, unetched beaker, dilute it to 200 ml, and heat it to boiling. Add dropwise a solution of titanous chloride (a 20 per cent solution of this reagent may be purchased) until the supernatant liquid appears slightly purple. If the solution is placed over a 100-watt light and stirred, observation of the end point is greatly facilitated. Boil the solution for two minutes and filter it. Wipe the walls of the beaker and also the stirring rod with a piece of ashless filter paper. Wash the filter and precipitated metal thoroughly with cold diluted sulphuric acid (2.5+97.5). Place the filter and contents in a 500 ml Erlenmeyer flask, add 10 ml of sulphuric acid, char gently, then heat the solution until vapors of sulphuric acid appear. Destroy the organic matter with nitric acid. Fuming nitric acid is preferable to the ordinary concentrated acid. If solution of the rhodium is not complete, that is, if some black specks remain unattacked, dilute the solution, filter it and return the filter to the flask. Wipe down the walls of the flask with a piece of ashless filter paper. Add 5 ml of fresh sulphuric acid, char the paper and destroy all organic matter with nitric acid. Heat the solution until heavy vapors of sulphuric acid are evolved. This treatment will insure complete solution of any remaining metal and will leave only a slight deposit of colorless silica.

Precipitate the rhodium a second time in the manner described above. Redissolve the rhodium as before, dilute the sulphuric acid solution with 20 ml of water and 10 ml of hydrochloric acid and boil the resulting solution for 15 minutes. This treatment is necessary to convert the rhodium to a form which will allow complete precipitation by hydrogen sulphide. Dilute the solution, now rose colored. Filter it and precipitate the rhodium by hydrogen sulphide from a boiling solution having a volume of from 400 to 500 ml. Filter the solution and wash the sulphide precipitate with cold diluted sulphuric acid (2.5+97.5) and finally with water. Place the filter with the sulphide precipitate in a porcelain crucible. Ignite the dried precipitate carefully in air. Ignite the oxidized residue in hydrogen, cool in hydrogen, and weigh as metallic rhodium.

3. RECOVERY AND DETERMINATION OF IRIDIUM

Dilute the combined filtrates from the precipitation of rhodium by titanous chloride to 800 ml. Cool the solution by placing the beaker in crushed ice. Add a chilled, filtered, freshly prepared solution of cupferron (6 per cent) in slight excess. Add some filter paper pulp, filter by suction and wash the titanium precipitate with chilled diluted sulphuric acid (2.5+97.5) containing some cupferron. The paper pulp is added to prevent the precipitate from becoming too densely packed. Return the precipitate to the beaker and add

nitric acid until the compound is mostly decomposed. Add 20 ml of sulphuric acid and heat until vapors of sulphuric acid appear. Destroy all organic matter with nitric acid. Dilute the resulting solution to 800 ml and repeat the precipitation of the titanium. The first cupferron precipitate will usually be contaminated by about 1 mg or less of iridium. Unite the two filtrates from the cupferron precipitations and evaporate until approximately 10 ml of sulphuric acid remains. Insure the destruction of all organic matter by adding nitric acid. Dilute the sulphuric acid solution with 20 ml of water and 10 ml of hydrochloric acid and boil the resulting solution for 15 minutes. Dilute the solution somewhat, filter it, and precipitate the iridium by hydrolysis. To do this, add a filtered solution of sodium bicarbonate until the acidity of the solution reaches a value of pH 6. Since the color of the solution will, in general, mask the color of the indicator, it is necessary to make the test on a drop of the solution clinging to the stirring rod. If a drop of brom cresol purple indicator solution (0.04 per cent) is colored faintly blue when it comes in contact with the drop of solution on the stirring rod, the solution possesses an acidity which will allow complete precipitation of the iridium. At this point, add 20 ml of a 10 per cent solution of sodium bromate and boil the solution for 20 to 25 minutes. Make sure, however, that sufficient bromate is present to oxidise all of the iridum to the quadrivalent state. Filter the solution and wash the precipitate thoroughly with a hot 1 per cent solution of ammonium chloride. Place the filter and precipitate of hydrated iridium dioxide in a porcelain crucible. Dry somewhat and moisten the contents of the crucible with a saturated solution of ammonium chloride. This is done to prevent deflagration of the hydrated dioxide on subsequent ignition in air. Ignite the filter and precipitate in air and then in hydrogen. Leach the metallic residue with diluted hydrochloric acid (1 + 5), transfer it to a filter and wash it with hot water. This precaution is taken to insure complete removal of soluble salts. Ignite the metallic residue in air. Finally, ignite the resulting oxidised metal in hydrogen, cool in hydrogen and weigh as metallic iridium.

The results of the determination of rhodium and of iridium, obtained by following the procedure of separation and of recovery which has just been outlined, with the exception that the iridium was precipated at pH 4, are given in Table 3. The result of one experiment, in which rhodium was twice precipitated by titanous chloride in the absence of iridium, is also included.

TABLE 3.—*Results of the analysis of solutions containing both rhodium and iridium*

No.	$(NH_4)_2RhCl_6$ taken 30.48 per cent Rh	Rhodium present	Rhodium recovered	Error	$(NH_4)_2IrCl_6$ taken 42.70 per cent Ir	Iridium present	Iridium recovered	Error
	g	*g*	*g*	*g*	*g*	*g*	*g*	*g*
25	0.1824	0.0556	0.0556	0.0000				
20-6	.1478	.0451	.0451	.0000	0.1722	0.0735		
60-48	.4444	.1355	.1354	−.0001	.2584	.1103		
66-54	.4732	.1442	.1442	.0000	.3309	.1413	0.1412	−0.0001
67-55	.3991	.1216	.1215	−.0001	.3804	.1624	.1622	−.0002
14-43	.2757	.0840	.0838	−.0002	.3092	.1320	.1320	.0000

NOTE.—A very faint greenish color was produced when the filtrates from the hydrolytic precipitation of iridium in Nos. 66-54 and 67-55 were tested for iridium. No iridium was detected in the filtrate from No. 14-43.

To make certain that the second precipitation by cupferron sufficed to separate all of the iridium from the titanium, the second cupferron precipitates were redissolved and the titanium reprecipitated. No trace of iridium was found in the filtrates from the third precipitation of the titanium, nor in the solutions of the third precipitates themselves.

The filtrates from the hydrolytic precipitations of the iridium were likewise tested. A small amount of iridium, not exceeding 0.1 mg, was found in the filtrates from Nos. 66–54 and 67–55.

The chemical examination of the recovered iridium for traces of rhodium is extremely difficult, as no sensitive test for rhodium is known. From the fact that rhodium was found to be completely precipitated by titanous chloride from pure solutions of rhodium and from the fact that the quantities of rhodium recovered from actual separation were identical with the quantities taken, it is reasonable to conclude that no significant amount of rhodium contaminated the recovered iridium.

The chemical examination of the separated rhodium for traces of iridium is simple because a sensitive test for iridium exists. A quantity of iridium, 0.1 to 0.2 mg, is sufficient to give a greenish cast to the yellow solution of rhodium in concentrated sulphuric acid. Since no iridium was detected either in the solutions of the rhodium which had been precipitated twice by titanous chloride or in the filtrates from the hydrogen sulphide precipitation of the rhodium, it was concluded that the recovered rhodium was not contaminated by iridium.

V. DISCUSSION OF THE METHOD

In the early experiments on the separation of rhodium from iridium the first precipitation was made from solutions of rhodium and iridium chlorides in diluted sulphuric acid (5+95) at room temperature. A considerable excess of titanous chloride was added and the solutions were filtered after definite periods of time. The precipitated metal was finely divided and partially passed through the filters. It was very difficult to observe the filtrates for escaped metal because of the intense color of the reagent. The large excess of titanous chloride appeared to cause the deposition of too great a proportion of the iridium. The deposition of iridium was even more pronounced when the solutions were heated in an attempt to coagulate the precipitates. Inasmuch as reprecipitation of the rhodium had to be made from a solution of the metal sulphates in diluted sulphuric acid, because of the method used to redissolve the precipitate, the first precipitation was also made from a similar solution in the later experiments. When both precipitations were made from a boiling solution of the metal sulphates and only a very slight excess of titanous chloride was added, it was found that the second precipitation of the rhodium completely eliminated the last trace of iridium.

Although the other four platinum metals must be absent at this stage of the general analysis, it was, nevertheless, desirable to know how they behaved toward titanous chloride. The reagent was added to solutions containing approximately 50 mg of each metal in 100 ml of diluted hydrochloric acid (5+95) at room temperature. Palladium

appeared to be precipitated immediately and platinum almost immediately. The brown color of ruthenium chloride was changed to deep blue, but no precipitation occurred when the solution was allowed to stand for one week. No precipitation occurred with a solution of chloroosmic acid even when it was allowed to stand for three weeks.

When solutions of rhodium, or of rhodium and iridium, are heated to heavy vapors of sulphuric acid, precaution must be taken to prevent the formation of insoluble compounds by local superheating. The formation of such compounds is easily avoided by keeping the hot sulphuric acid solution in constant motion.

The essential feature which makes the scheme proposed by Wada and Nakazono workable is a method by which the precipitated rhodium can be redissolved. A few comments regarding the technic of the operation appear worthy of emphasis. An Erlenmeyer flask should be used in preference to a beaker or to a Kjeldahl flask. With a beaker, there is danger of mechanical loss of material, particularly at the danger of mechanical loss of material, particularly at the stage where the last traces of moisture are being eliminated. The drops of condensed steam on the under side of the cover glass fall into the hot sulphuric acid and cause violent spattering. With a Kjeldahl flask, it is extremely difficult to wipe down the particles of undissolved metal from the walls. If this latter precaution is not observed, the results for the recoveries of rhodium will invariably be low by amounts up to about 1 mg.

The metallic rhodium, obtained in the second precipitation with titanous chloride, must not be ignited directly because it is always contaminated by silica, introduced through the titanous chloride and possibly from the glassware, and by a small amount of titanium. Consequently, the rhodium is again dissolved and precipitated by hydrogen sulphide. It was not found possible to precipitate the rhodium completely by hydrogen sulphide from solutions of the metal sulphate in sulphuric acid. This same difficulty has often been observed in this laboratory with solutions prepared by dissolving the product of bisulphate fusions of rhodium. A solution of the rhodium can be prepared, however, by adding diluted hydrochloric acid (1+2), equal to three times the volume of the concentrated sulphuric acid solution, and boiling it. The yellow color of the sulphate solution then changes to rose red, which is the same as the characteristic color of rhodium chloride. No difficulty attends the precipitation of rhodium from the solution so treated.

The determination of rhodium and of iridium can be greatly simplified and the titanium precipitations avoided if the solution can be divided conveniently into aliquot parts. Incidental experiments showed that rhodium is completely precipitated as an olive-green hydrated dioxide at pH 6 when bromate is present. Since iridium is precipated quantitatively under the very same conditions, the two can be precipitated together and finally recovered as a metallic mixture. In addition, rhodium must be determined separately on a different portion by precipitation with titanous chloride in the manner described in the recommended procedure.

The method which has been described in this paper is designed for the separation of rhodium from iridium and for the determination of these metals when other elements are absent. It will constitute a part of a general scheme for the analysis of the platinum group and will follow the procedures for the separation of osmium, ruthenium, platinum, and palladium.

WASHINGTON, July 11, 1932.

RP490

THE ISOELECTRIC POINT OF SILK

By Milton Harris [1]

ABSTRACT

Suspensions of silk in buffer solutions of different pH were prepared by grinding the dry silk fibroin to a fine powder and shaking it in the buffer solution.

Colloidal solutions of silk were prepared by dissolving the silk fibroin in a 50 per cent lithium bromide solution and dialyzing it to remove the salt. To the solutions were added known buffer mixtures and a small amount of purified quartz powder.

Electrophoretic measurements of the suspensions of silk and of the dissolved silk adsorbed on the quartz particles gave an isoelectric point at pH 2.5.

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I. INTRODUCTION

A colloidal (or other) particle is said to be at its isoelectric point when the particle is electrically neutral with respect to its surrounding medium. This point is usually defined in terms of some property such as the pH of the medium. For an amphoteric substance the acidic and basic ionizations are equal at this point.

The most direct method of determining the isoelectric point is to define the conditions under which the particles do not move in an electric field. Such movement is called electrophoresis.

Electrical mobility measurements have been used in the determination of the isoelectric point of wool.[2] It is the purpose of this paper to present similar measurements of silk.

Satisfactory suspensions of wool could only be prepared mechanically; that is, by grinding the wool to a fine powder, whereas silk may be readily prepared in suspensions and in colloidal solution.[3] Abramson[4] has shown that when quartz particles are suspended in dilute protein solutions, the protein is absorbed on the surface of the quartz particle, and the latter assumes the electrokinetic properties of the protein. This suggested a method for determining the isoelectric point of the dissolved silk.

II. PROCEDURE

The electrophoresis apparatus and methods used in this work were the same as used in the determination of the isoelectric point of wool.[5]

[1] Research associate representing the American Association of Textile Chemists and Colorists.
[2] M. Harris, The Isoelectric Point of Wool, B. S. Jour. Research vol. 8, pp. 779–786, 1932.
[3] M. Harris and T. B. Johnson, Study of Silk Fibroin in the Dispersed State, Ind. & Eng. Chem., vol. 22, p. 965, 1930.
[4] H. A. Abramson, The Adsorption of Serum Proteins by Quartz and Paraffin Oil, J. Gen. Physiol., vol. 13, pp. 169–177, 1929.
[5] See footnote 2.

The silk was purified as follows: A sample of raw China silk was boiled successively in three ½ per cent solutions of soap for 20 minutes each. It was then washed with distilled water, dilute ammonia, dilute hydrochloric acid, and finally repeatedly with distilled water, at 60° C. It was then air dried for 24 hours.

One portion of the purified silk was ground in a Wiley mill. The size of the silk particles varied from 5 μ to 30 μ. A small amount of the ground silk was shaken vigorously with distilled water, and the larger particles allowed to settle. The upper portion was carefully decanted and used for one set of measurements.

A second portion of approximately 5 g of the silk was dissolved in 50 ml of a 50 per cent solution of lithium bromide at about 80° C. The solution was diluted to 200 ml, treated with a few drops of toluene to prevent bacterial action and dialyzed in a cellophane bag against distilled water until it gave no test for LiBr. Approximately 20 ml of the resultant solution of silk was diluted to 200 ml and the purified quartz particles described below were added. The silkcoated quartz thus obtained was used for the second set of measurements.

Quartz particles (size range 5 μ to 20 μ) were purified as described by Abramson.[6] Crude quartz powder was heated with a cleaning solution consisting of concentrated sulphuric acid saturated with sodium dichromate and diluted with water, for about 30 minutes. The particles were allowed to settle and the excess acid carefully decanted. A large amount of distilled water was added and the quartz suspension was filtered. The powder was washed with distilled water and then boiled with an excess of normal hydrochloric acid and allowed to settle. It was again filtered and washed with water for 48 hours.

In making the suspension to be studied, a very small amount of the quartz powder was added to the silk solution, which made it faintly cloudy.

Portions of each of these suspensions were mixed with equal volumes of the following buffer mixtures[7] with double the usual concentrations: pH 1.4 to 2.2, potassium chloride-hydrochloric acid mixture; pH 2.4 to 3.8, acid potassium phthalate-hydrochloric acid mixture; pH 4.0 to 6.0, acid potassium phthalate-sodium hydroxide mixtures.

III. DISCUSSION OF RESULTS

The mobilities of the particles recorded in the following table are the averages calculated from 10 observations.

TABLE 1.—*Electrophoretic mobility of silk (relative velocity)*

pH	Ground silk	Dissolved silk+ quartz	pH	Ground silk	Dissolved silk+ quartz
1.42	+1.20	+1.14	2.86	−0.48	−0.36
1.84	+.73	+.79	3.00	−.57	−.58
2.13	+.48	+.37	3.33	−.88	−.82
2.30	+.24	+.26	3.69	−1.15	−1.27
2.54	−.14	+.11	4.21	−1.37	−1.40

[6] See footnote 4, p. 557.
[7] M. Clark, The Determination of Hydrogen Ions, pp. 106–107, Williams & Wilkins Co.

These data are shown in graphical form in Figure 1. The isoelectric point of silk obtained from the pH-mobility curve is pH 2.5. This value is in good agreement with the values obtained by Hawley and Johnson [8] and by Harris and Johnson [9] but not in agreement with those obtained by Meunier and Rey [10] and Denham and Brash.[11]

Hawley and Johnson employed a U tube electrophoresis cell and obtained values in the range from pH 1.4 to 2.8. Since the diameter of the cell was comparatively large, diffusion and convection currents

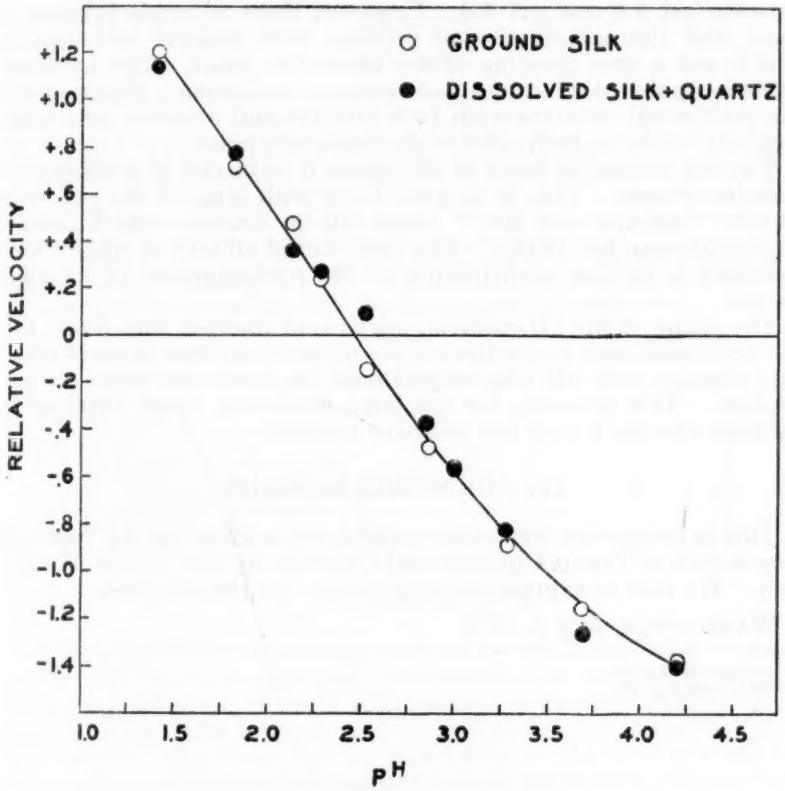

FIGURE 1.—*pH-mobility: curve for silk*

made it difficult to detect small changes in protein concentration in the anode and cathode regions.

Harris and Johnson prepared solutions of silk fibroin by dissolving the degummed silk in concentrated aqueous solutions of lithium bromide and calcium thiocyanate. From solubility and viscosity measurements, values ranging from pH 2.1 to pH 2.4 were obtained.

[8] T. G. Hawley and T. B. Johnson, The Isoelectric Point of Silk Fibroin, Ind. & Eng. Chem., vol. 22, pp. 297–299, 1930.
[9] M. Harris and T. B. Johnson, Study of the Fibroin from Silk in the Isoelectric Region, Ind. & Eng. Chem., vol. 22, pp. 539–542, 1930.
[10] L. Meunier and G. Rey, Determination du point isoelectrique de la laine et de la soie, Compt. rend, vol. 184, p. 285, 1927.
[11] W. Denham and W. Brash, The Isoelectric Point of Silk Fibroin, J. Textile Inst., vol. 18, p. T520–525, 1927.

Meunier and Rey reported an isoelectric point for silk at pH 4.2. Their results were based on the swelling of the fiber in solutions of varying hydrogen ion concentration. The curve which they obtained is flat in the region from about pH 3 to pH 6 and shows no well defined point of minimum swelling.

Denham and Brash studied the combination of acidic and basic radicals with the silk fibroin when the latter was placed in solutions of acids, bases, and salts. They, too, were unable to obtain a definite isoelectric point and concluded from their experiments that it lies between pH 3.6 and pH 4.0. However, there is ample evidence to show that the combination of proteins with positive and negative ions is not a true measure of the isoelectric point. The isoelectric point is a point of minimum and not zero ionization. Consequently the protein will combine with both positive and negative ions within a certain range on both sides of the isoelectric point.

The low isoelectric point of silk shows it to be one of the most acid proteins known. This is in accordance with some of the properties of silk. Meunier and Rey [12] found silk to contain only 7 parts of amino nitrogen per 10,000. The pronounced affinity of silk for basic dyestuffs is further confirmation of the predominance of its acidic nature.

The shape of the pH-mobility curve is of interest, and shows that the acidic and basic properties are less pronounced than those of wool.[13] Any changes with pH which occur near the isoelectric point are only gradual. This accounts for the large isoelectric range obtained by workers who have used less sensitive methods.

IV. ACKNOWLEDGMENT

This investigation was made possible by a grant to the American Association of Textile Chemists and Colorists by the Textile Foundation. We wish to express our appreciation for the aid given.

WASHINGTON, July 8, 1932.

[12] See footnote 10, p. 559.
[13] See footnote 2, p. 557.

RP491

EFFECTIVE APPLIED VOLTAGE AS AN INDICATOR OF THE RADIATION EMITTED BY AN X-RAY TUBE

By Lauriston S. Taylor, G. Singer, and C. F. Stoneburner

ABSTRACT

A previous study [1] suggested a parallelism between the applied effective voltage and the emission of an X-ray tube. The investigation has been carried further under more carefully controlled conditions. It is found for two mechanical rectifiers and one "constant potential" generator that the X-ray emission per effective (root-mean-square) milliampere of tube current is about the same for all generators operating at the same effective (r. m. s.) voltage (the radiation passing through the same filter in all cases). Thus it becomes possible to express all radiations in terms of that excited by constant potential. This leads to a simplification in the description and reproduction of irradiation conditions in biological work. Although the study has been limited to three generators, it is believed that they are sufficiently typical to warrant generalization.

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I. INTRODUCTION

In a recent study the energy emitted by an X-ray tube, as measured by an ionization chamber, was found to be very different when excited by different types of high voltage generators furnishing the same average tube current and peak voltage (as measured by a sphere gap). But it was further found that for the same average currents and the same effective voltage [2] of the generators, the emission, as measured by the ionization chamber, is approximately the same.

The total energy in an X-ray spectrum devoid of characteristic lines varies as the square of the instantaneous applied voltage, and hence for a known voltage wave form the total energy and its wavelength distribution, for the period of a complete cycle, is calculable. Because of the presence of tungsten line radiation about 70 kv, it is not yet practicable to predict the total X-ray energy by integrating over one cycle of the voltage wave. In the present work the X-ray emission per unit tube current, as it varies with peak voltage, with average voltage, and with effective voltage per unit tube current is given for more carefully controlled and wider ranges of conditions. This is expressed in terms of the X-ray emission per milliampere.

[1] L. S. Taylor and K. L. Tucker, B. S. Jour. Research, vol. 9 (R P 475), p. 333, 1932.
[2] Effective voltage is mathematically the same as root-mean-square (r. m. s.) voltage.

II. APPARATUS

Thus far three generators have been used, designated by *A*, *B*, and *C* as in the preceding work.[3] *A* is a full wave mechanical rectifier having a single high tension transformer, and rectifying over approximately 30 degrees of cycle; *B* is also a full wave mechanical rectifier but with a divided high tension transformer (two transformers in a single tank), and rectifying over approximately 20 degrees of the cycle; *C* is a valve-tube-condenser ripple potential[4] generator (so-called "constant potential") having a ripplage of about 2 per cent per milliampere. The three generators could be interchangeably connected to the same X-ray tube.

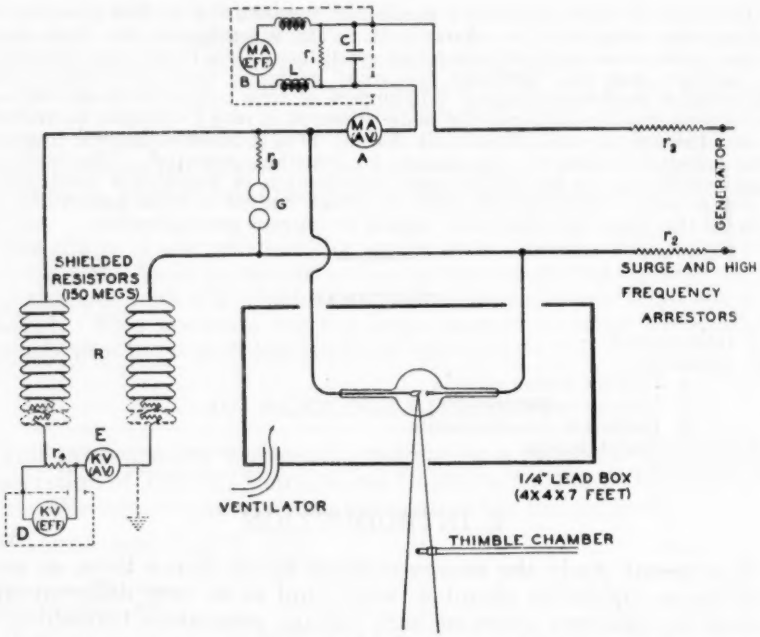

FIGURE 1.—*Apparatus showing voltage and current measuring equipment*

1. CURRENT MEASUREMENTS

The arrangement of the apparatus is indicated in Figure 1. Average current through the tube is measured in the usual manner by a d. c. milliammeter *A;* and the effective current by an a. c. milliammeter, *B*. For this purpose a thermo milliammeter alone was available. This was protected from high-frequency oscillations by iron core chokes, *L*, having a d. c. resistance of a fraction of an ohm; a noninductive resistor, *r*, of about 10,000 ohms, and a 1/20 μf capacitor, *C*.

[3] See footnote 1, p. 561.

[4] The term "constant potential" has been used loosely to describe the potential supplied by kenotron of other valve tube rectification. A more accurate designation of a voltage which is not constant in fact but fluctuates slightly about a certain average value is "ripple voltage." Thus by a "ripple quantity" (potential or current) is meant a simple periodic quantity $y = V_0 + V_1 \sin(\omega x + \alpha_1) + V_2 \sin(2\omega x + \alpha_2) + \cdots$ in which the constant term (V_0) is so large that all values of the quantity are positive (or negative). The amount of ripple ("ripplage" or "ripplance") in a ripple quantity is the ratio of the difference between the maximum and minimum values of the quantity to the average value. These definitions are under consideration by the Committee on Electrical Definitions of the American Standards Association under the sponsorship of the A. I. E. E.

Since the resistance of the meter, B, was only about 20 ohms, this shunt system served as a very effective filter against high-frequency oscillations in the high-tension system, without affecting the sensitivity.

Excessive high-frequency oscillation when using the mechanical rectifiers caused difficulty in peak-voltage measurements with the sphere gap, but this was largely eliminated by placing two 1/2-megohm inductively wound surge resistors, r_2, immediately next to the rectifier switches, giving smoother operation of the equipment and more consistent peak voltage measurements. After raising the generator voltage sufficiently to compensate for the potential drop across the resistors, it was found that their presence did not alter the tube output in any way.

With generator C, the same resistors were used for the purpose of limiting the current in case of slight tube gassing or when using a sphere gap for measuring the voltage. It was found that they raised very materially the voltage limit at which a given tube would operate satisfactorily.

2. VOLTAGE MEASUREMENTS

Peak voltage of all three generators was measured by the gap between 12.5 cm spheres, protected by a water resistance r_3, of the order of 5 megohms to prevent heavy arcing at the gap and consequent tripping of circuit breakers.

Average voltage was measured by means of a d. c. microameter, E, in a series with a shielded high voltage resistor of 150 mehohms,[5] the meter being at the center of the resistance so as to be at or near ground potential.[6]

Effective voltage was measured by means of a 150-volt calibrated Kelvin multicellular electrostatic voltmeter, D, shunted across a resistance, r_4, of 75,000 ohms. Since its potential was likely to be different from ground, it was necessary to shield it by a metal case having the same potential as one of its terminals.

It should be stated here that the insertion of the high-voltage resistor, R, across the line has no noticeable influence upon the operation of the high-tension generators because the current it shunts off is very small. This fact is of course essential, since a wave form very different from that under normal operating conditions may otherwise result.

3. RADIATION MEASUREMENTS

The X-ray emission was measured by means of a thimble chamber, kept in a fixed position with respect to the tube throughout the study. The beam was in all cases filtered by 0.525 mm of copper, the wall effect of the chamber being negligible for the transmitted radiation.

No other determination of radiation quality was undertaken, as the previous study[7] indicated what was to be expected under the operating conditions employed here, namely, all beams having the same effective voltage and filtration and giving equal intensities have approximately the same quality (whether expressed in the half-value layer of copper, copper absorption coefficient, or effective wave length).

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[5] L. S. Taylor, B. S. Jour. Research, vol. 5 (RP217), p. 609, 1930.

[6] The voltage on the high-tension conductors is seldom divided equally above and below ground potential, although the error in measurement introduced by grounding the resistor at the center is very small.

[7] L. S. Taylor and K. L. Tucker. See footnote 1, p. 561.

III. EXPERIMENTAL RESULTS

In this study, to eliminate the effect of variation in operation, simultaneous values were obtained for (1) average current, (2) effective current, (3) peak voltage, (4) average voltage, (5) effective voltage, and (6) X-ray tube output for a constant filteration of 0.525 mm of copper, the average current (the quantity measured in practice) serving as independent variable.

In Figure 2, groups *A* and *B* show the tube emission, expressed in terms of the ionization current per average milliampere (I/ma (average)), as a function of peak voltage for generators *A* and *B*, respectively, and for different tube currents, 2, 3, 4, and 5 ma. With generator *B* it is seen that for a given peak voltage, the value of I/ma (average) varies from 10 to 15 per cent in changing the operating

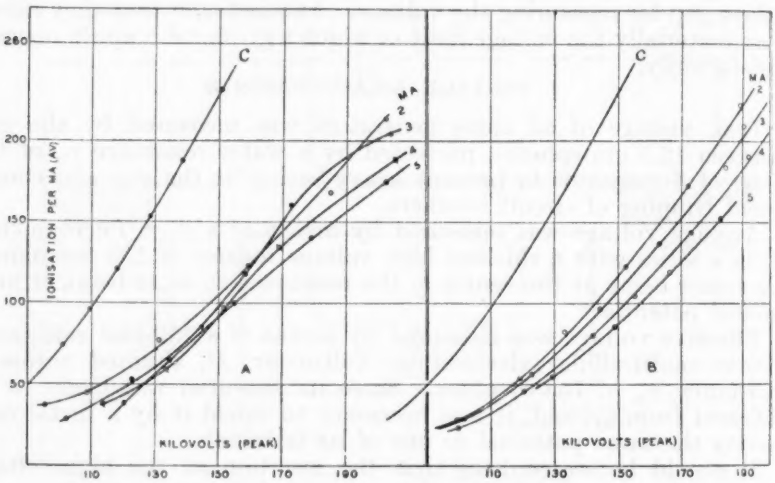

FIGURE 2.—*Relationship between X-ray tube emission per average milliampere, and the applied peak voltage*

A, *B*, mechanical rectifiers; *C*, constant potential.

tube current by 1 mA. This is not unexpected since the generator wave form depends to a large extent upon the power drawn from the generator. It is obvious from these curves that it may be very misleading to attempt to deduce the emission of an X-ray tube from current and peak voltages alone. For generator *A*, I/ma (average) varies erratically with peak voltage under different operating currents.

Figure 2, curve *C* in both groups is from generator *C* ("constant potential") for a tube current of 4 ma. Since the peak voltage of this generator does not vary appreciably with tube current (average voltage being kept constant), a single curve embodies the results. It is seen that for the same peak voltage there is a large difference between the X-ray emission of generator *C* (curve *C*) on the one hand and that of generators *A* and *B* (curves *A* and *B*) on the other. To obtain the same X-ray emission from generators *A* and *B* as from generator *C*, the peak voltage of *A* and *B* must be very much larger than that of *C*, depending upon the operating current.

If, for the same radiations plotted in Figure 2, we plot instead the ionization per average milliampere against the average voltage, corresponding curves, *A*, *B*, and *C* in Figure 3 are obtained. It will be noted that I/ma (average) again varies with the tube current. In the case of generator *A* the values of *I*/ma (average) vary from about 2 to 8 per cent in changing the operating current by 1 ma. This percentage change becomes smaller, however, in going to higher average voltages, whereas, when the potential is measured in peak kilovolts, the changes become larger at higher voltages.

In the case of generator *B* the same general results obtain. The variation of *I*/ma (average) with tube current at a given average voltage is, however, much greater at lower potential than for *A* while at higher potentials it is about the same.

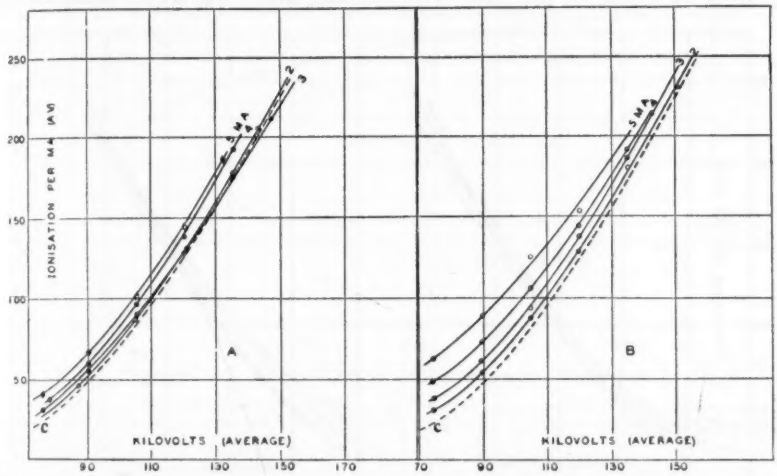

FIGURE 3.—*Relationship between X-ray tube emission per average milliampere, and the applied average voltage*

A, *B*, mechanical rectifiers; *C*, constant potential.

It is seen that, while the curves for *A* and *B* differ with tube current, they all lie in the region of curve *C* (dashed) as contrasted to the corresponding curves of Figure 2 for peak voltages. Thus, if the current and voltage for all three generators be measured in terms of average milliamperes and average kilovolts (that is, by using d. c. instruments), the tube emission per milliampere is in all cases of the same order of magnitude.

Using effective milliamperes and effective kilovolts, curves for generators *A*, *B*, and *C* for the X-ray emission per effective milliampere are given in Figure 4.

It should be pointed out that for the comparatively small ripplage present in the voltage of generator *C*, the difference between the average and effective voltage is so small that it may be neglected. Likewise their variation with tube current is negligible; hence, a single curve for *I*/ma (effective) gives a satisfactory basis of comparison.

In the case of generator *A* the change in emission per milliampere, as the operating current is varied, is present and somewhat erratic as

in the case of the peak voltage curves. The percentage change, however, is the least of the three cases given. Similarly in the case of generator *B* the change is present, but again to the least degree.

Of prime importance, however, is the fact that the curves (fig. 4) for both generators *A* and *B* lie very closely along the curve for constant potential—much more closely at the higher voltages than those in Figure 3 for average current and voltage measurements. It is concluded that, for equal effective X-ray tube currents and equal effective voltages, the emission per milliampere will be sufficiently near the same with all three generators, for the effective current and voltage to be used as characteristic of the X-ray emission.

Since the emission per milliampere for all strictly constant potential generators is the same, it is logical that it be referred to as a base. By means, then, of the effective current and effective voltage mea-

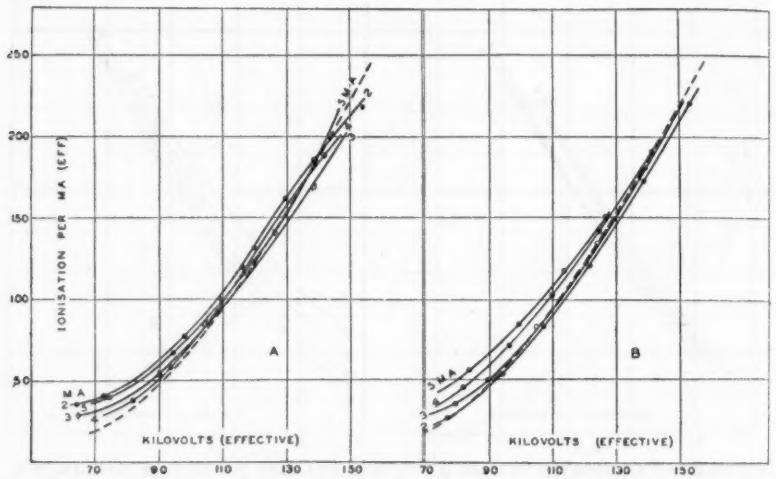

FIGURE 4.—*Relationship between X-ray tube emission per effective milliampere, and the applied effective voltage*

A, *B*, mechanical rectifiers; broken line curve, constant potential.

surements described, it is possible to relate consistently the X-ray emission excited by the various types of generators.

It is possible to trace the residual variation in X-ray emission per milliampere at lower voltages with the operating current, largely to the current-voltage characteristics of the X-ray tube. This will account also for the divergence from the constant potential base line. Figure 5 shows, for various applied constant potentials, the tube current curves for three values of the filament current, I_f. It is seen that, since the tube current is still increasing about 5 per cent per 30 kilovolts at 120 kilovolts, saturation is not attained. Consequently, with the application of a varying voltage to the tube, the effective current is bound to depend upon the voltage wave form to a varying degree.

This is illustrated in Figure 6 where curves *a* and *b* are two hypothetical tube current characteristics, the second of which is ideal in that it reaches saturation at a comparatively low voltage. Curves *D*, *E*, and *F* represent three types of generator voltage wave form

having the same effective voltage, e, which, when applied to tubes having characteristics a and b, produce the tube current wave forms a' and b', respectively, for each associated voltage wave. In each of

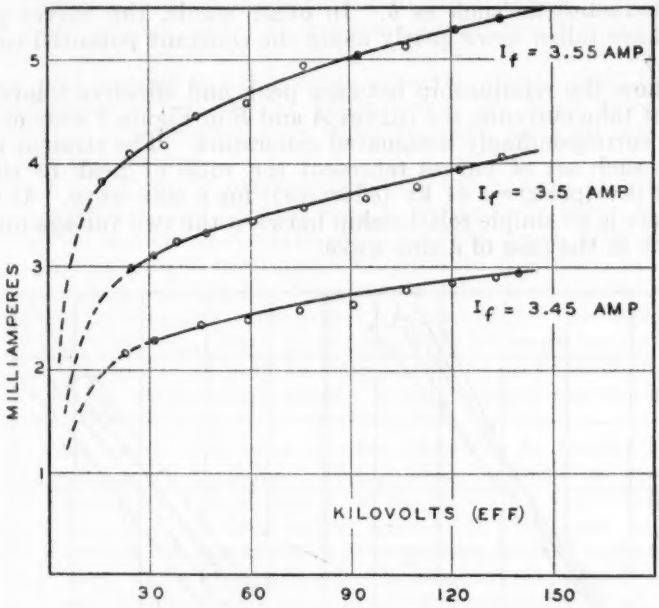

FIGURE 5.—*Tube current—tube voltage characteristics*

the cases it is seen that the effecitve current i_a for tube characteristic a is lower than the effective current i_b for characteristic b. Moreover, the magnitude of this difference depends upon the generator voltage wave form as shown.

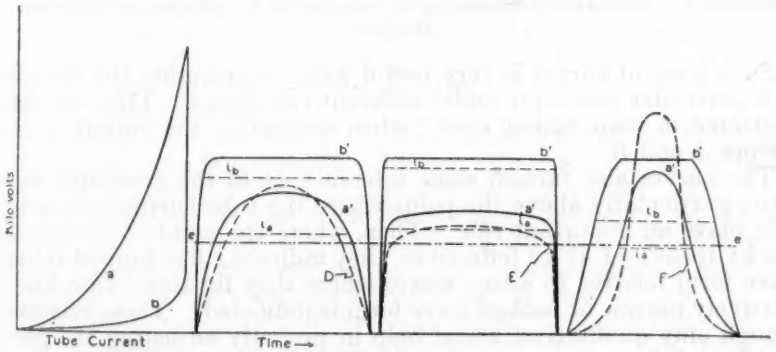

FIGURE 6.—*Effect of tube characteristic and generator wave form on the effective tube current*

To compare the explanation above with the results found, we note that the experimentally determined tube characteristics in Figure 5 are similar to a in Figure 6; hence, the tube current measured in

effective amperes is less than it would have been had the tube reached saturation at as low voltage as for characteristic *b*.

In Figure 4 the emission per effective milliampere—which is plotted against effective kilovolts—would accordingly have been less with an ideal characteristic such as *b*. In other words, the curves plotted would have fallen more nearly along the constant potential curve *C*. (Fig. 4.)

To show the relationship between peak and effective kilovolts for different tube currents, the curves *A* and *B* in Figure 7 were obtained for the correspondingly designated generators. The straight dashed lines in each set of curves represent the ratio of peak to effective voltage (kv (peak) = 1.41 kv (effective)) for a sine wave. It is seen that there is no simple relationship between the two voltage measurements as in the case of a sine wave.

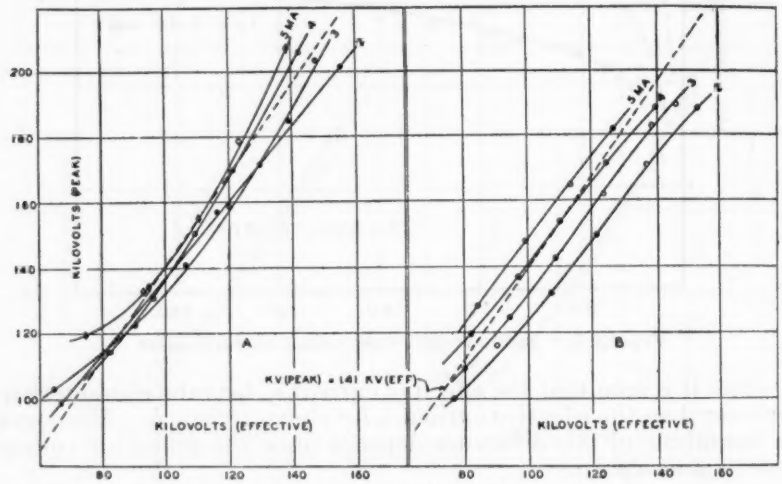

FIGURE 7.—*Relationship between peak and effective kilovolts for two mechanical rectifiers*

Such a set of curves is very useful when interpreting the behavior of a particular generator under different conditions. This was demonstrated in some earlier work [8] when comparing the output of generators *A* and *B*.

The curves also furnish some inference as to the generator wave form, particularly above the point where the tube current characteristic plays an important rôle. Thus, where the points lie below the line kv (peak) = 1.41 kv (effective), they indicate a flat-topped voltage wave form relative to a sine wave; where they lie above that line, a relatively narrow or peaked wave form is indicated. These relations, though only qualitative, are of help in properly adjusting the phase position of the switches on a mechanical rectifier for optimum X-ray tube emission.

[8] See Figure 16 with explanation in paper by L. S. Taylor and K. L. Tucker. (See footnote 1, p. 561.)

IV. DISCUSSION

There has been considerable confusion in interpreting the physical magnitudes involved in the therapeutic use of high-voltage X rays. The greatest single factor contributing to this confusion has been the voltage measurement, since it has been sometimes assumed that a given X-ray tube, activated by the same voltage (by sphere gap measurement) and passing equal average currents, should yield the same X-ray emission for all similar generators. We have shown here, however, that the emission may differ by ±20 per cent under supposedly like conditions.

Although a difference existing between mechanical and constant potential rectifiers has been generally recognized, there has been uncertainty as to any exact relationship between them, with the result that few attempts have been made to correlate treatment factors for the two machines. There has been even a belief that the radiation of one could not be clinically reproduced by the other. The experiments described here show that both generators may be made to produce the same emission (as far as may be deduced from absorption measurements in copper or paraffin) when the tube potentials are properly adjusted.

The present study has been limited thus far to mechanical and "constant potential" rectifiers. While it is believed by some that mechanical rectifiers will probably be displaced by valve-tube rectifiers, the study is of no less value, since with the great variety of valve-tube circuits in use there is an equal variety of voltage wave forms produced, none of which may be readily correlated as far as they affect the X-ray output of a tube. For example, in addition to "constant potential" there will be half-wave, full-wave, and polyphase rectifiers and voltage doubling circuits, such as the La Tour and Villard systems. In some of these the wave form depends upon load to a greater extent than in others and, as a consequence, measurements of peak voltage alone will lead to similar discordance now encountered in mechanical rectifiers.

This study reveals that, when the generator potential is measured in effective kilovolts, the X-ray emission of a tube is equivalent to that produced by very nearly the same constant potential. It is thus possible to express the emission in terms of that obtainable from a constant potential source.

Expressing tube potential in effective kilovolts simplifies the method of expressing radiation quality. For example, when describing radiation quality in terms of the "half-value layer of copper" it is recognized as necessary to also state the voltage. However, as voltages are now measured, even this is inadequate due to the effect of wave form. To correctly indicate quality by the usual absorption methods, the effective voltage should be stated—not the peak voltage.

The cordial cooperation of the Radiological Research Institute and of the American X-ray equipment manufacturers in this work has been very helpful.

WASHINGTON, June 17, 1932.

RP492

COLUMN CURVES AND STRESS-STRAIN DIAGRAMS

By William R. Osgood

ABSTRACT

The only important column formula which rests on a strictly theoretical basis is the Considère-Engesser formula, which includes the Euler formula as a special case. Attempts have been made to underpin by a general theoretical foundation other essentially empirical formulas, notably the Rankine formula; but these attempts have not been successful. It would be very satisfying, however, if these empirical formulas could be shown to be reasonable special forms of the Considère-Engesser formula. Any column formula for centrally loaded columns is a special case of the Considère-Engesser formula provided the compressive stress-strain diagram has a certain definite shape. The present paper examines a few of the commonest types of empirical formulas and determines the shape of the stress-strain diagram in each case which makes them compatible with the Considère-Engesser theory.

The only column formula which rests on a strictly theoretical basis and which at the same time is of practical importance, in the sense that tests confirm the theory, is the Considère-Engesser formula,[1] which includes the Euler formula as a special case. Attempts have been made to underpin by a general theoretical foundation other formulas, essentially empirical, notably the Rankine formula; but no successful attempt has yet been made. It would be very satisfying, however, if these empirical formulas could be shown to be reasonable special forms of the Considère-Engesser formula. Any column formula for centrally loaded columns is a special case of the Considère-Engesser formula, provided the compressive stress-strain diagram of the material has a certain definite shape. It is the purpose of the present paper to examine a few of the commonest empirical formulas and to determine the necessary shape of the stress-strain diagram in order that these formulas may be compatible with the Considère-Engesser theory. A somewhat similar investigation has been carried out by P. M. Frandsen,[2] but he refers the empirical formulas back to the Engesser formula.[3]

[1] Developed in 1889 and the years following by A. Considère, Fr. Engesser, and F. Jasinski; re-presented independently by Theo. v. Kármán, Mitteilungen über Forschungsarbeiten, Verein deutscher Ingenieure, Heft 81, Berlin, Julius Springer, 1910, and by R. V. Southwell, Engineering, vol. 94, p. 249, London, Aug. 23, 1912.

[2] Den Teknisk Forenings Tidsskrift, Hæfte 19, p. 139, Copenhagen, Sept. 15, 1920.

[3] Zeitschrift des hannoverischen Architekten- und Ingenieur-Verein, vol. 35, p. 455, 1889.

The following notation will be used:

P = the load on the column at failure by buckling.

A = the cross-sectional area of the column.

$\sigma = \frac{P}{A}$ = the average normal stress on the cross section at failure.

l = the "free length" of the column, the distance between two successive points of inflection of the center line.

i = the least radius of inertia or radius of gyration of the cross section of the column, measured parallel to the plane of bending.

E = the modulus of elasticity of the material of the column.

E' = the "tangent modulus" at the stress σ; that is, E' is the slope of the compressive stress-strain diagram at the stress σ.

$\overline{E} = \frac{E'I_1 + EI_2}{I}$, where I_1 is the moment of inertia about the axis of average stress of the part of the cross-sectional area which suffers an increase of stress at the instant of failure of the column, I_2 is the moment of inertia about the axis of average stress of the part of the cross-sectional area which suffers a decrease of stress at the instant of failure of the column, and $I = Ai^2$ is the moment of inertia of the total cross-sectional area of the column about the gravity axis perpendicular to the plane of bending; the position of the axis of average stress is defined by the relation $E'S_1 = ES_2$, where S_1 and S_2 are the statical moments about the axis of average stress, respectively, of the two parts of the cross-sectional area just mentioned in connection with I_1 and I_2.

ϵ = the strain due to the stress σ.

σ_u = the short-column strength of the material, to be taken as the yield point in the case of ductile materials. (See Appendix II.)

$e = \frac{E\epsilon}{\sigma_u}$.

$s = \frac{\sigma}{\sigma_u}$.

σ_p = the stress above which Euler's formula ceases to apply strictly the proportional limit of the material, but practically likely to be considerably above the actual proportional limit.

$s_p = \frac{\sigma_p}{\sigma_u}$,

$\lambda = \frac{1}{\pi}\frac{l}{i}\sqrt{\frac{\sigma_u}{E}}$.

C_n, C_R, constants.

The assumptions underlying the Considère-Engesser theory are that the material is homogeneous, cross sections remain plane, the stress-strain relation for increasing strain is the same as that given by the stress-strain diagram, the stress-strain relation for decreasing strain is given by a line parallel to the tangent to the stress-strain diagram at the origin, the axis of the column is straight, the cross

section of the column is uniform throughout the free length, and the loading is axial.

The Considère-Engesser formula may be written

$$\sigma = \frac{\pi^2 \bar{E}}{\left(\frac{l}{i}\right)^2} \tag{1}$$

In order that any empirical formula expressible as

$$\frac{l}{i} = f(\sigma) \tag{2}$$

give the same relation between σ and $\frac{l}{i}$ as the Considère-Engesser formula, we must have

$$\bar{E} = \frac{\sigma}{\pi^2}\left(\frac{l}{i}\right)^2 \tag{3}$$

where $\frac{l}{i}$ is given by (2). The stress-strain diagram must satisfy this equation.

$\bar{E}$ is a function not only of the slope of the stress-strain diagram at (ϵ, σ) but also of the shape of the cross section, and no general reduction of equation (3) is possible. Fortunately, however, the effect of the shape of the cross section on the value of $\bar{E}$ does not vary greatly for cross sections ordinarily used which have an axis of symmetry perpendicular to the plane of bending.[4] It can be shown that $\bar{E}$ is smaller for the idealized H section (negligible web, flanges thin compared to distance between them) with the plane of bending normal to the flanges than for any other section with the symmetry just mentioned. Consequently, if $\bar{E}$ for the H section is used, equation (1) will give results on the safe side for all symmetrical sections, and equation (3) may be reduced with the assurance that the results obtained represent limiting values for such sections. The value of $\bar{E}$ for the idealized H section is [5]

$$\bar{E} = \frac{2\,E\,E'}{E + E'} \tag{4}$$

which, substituted in equation (3), with $E' = \frac{d\sigma}{d\epsilon}$, gives

$$\sigma = \frac{\pi^2}{\left(\frac{l}{i}\right)^2} \cdot \frac{2}{\frac{d\epsilon}{d\sigma} + \frac{1}{E}} \tag{5}$$

and this is the equation of the stress-strain curve if equation (2) is to represent a theoretically possible column formula.

[4] See Appendix I.
[5] Kármán (see footnote 1, p. 571).

Instead of integrating equation (5) for various functions $\frac{l}{i}=f(\sigma)$, it is preferable for comparative purposes to introduce the nondimensional variables [6]

$$e=\frac{E\epsilon}{\sigma_u}, s=\frac{\sigma}{\sigma_u}, \lambda=\frac{1}{\pi}\frac{l}{i}\sqrt{\frac{\sigma_u}{E}} \tag{6}$$

In terms of these quantities equations (1) and (5) become

$$s=\frac{1}{\lambda^2}\frac{\bar{E}}{E} \tag{7}$$

and

$$s=\frac{1}{\lambda^2}\cdot\frac{2}{\frac{de}{ds}+1} \tag{8}$$

where in the latter equation λ is a given function of s; (7) is the equation of a curve obtained from the column curve by dividing the average stresses by σ_u and the slenderness ratios by $\pi\sqrt{\frac{E}{\sigma_u}}$, and (8) is the equation of a curve obtained from the stress-strain curve by dividing the stresses by σ_u and the strains by $\frac{\sigma_u}{E}$.

In the Euler range, for which $\bar{E}=E$, equation (7) reduces to

$$s=\frac{1}{\lambda^2} \tag{9}$$

and equation (8) becomes, with the use of equations (6)

$$s=e \tag{10}$$

For values of s above s_p; that is, above the Euler range, for a continuous stress-strain diagram the solution of (8) becomes

$$e=2\int_{s_p}^{s}\frac{ds}{s\lambda^2}-s+2s_p \tag{11}$$

The reduced stress-strain diagram represented by equations (10) and (11) will now be considered for some empirical column formulas.

The parabolic or hyperbolic type of formula.—A common type of formula is one of the form

$$\sigma=\sigma_u\left[1-C_n\left(\frac{l}{i}\right)^n\right] \tag{12}$$

If

$$C_n=\frac{2}{n\pi^n}\left(\frac{n}{n+2}\right)^{1+\frac{n}{2}}\left(\frac{\sigma_u}{E}\right)^{\frac{n}{2}}$$

the curve represented by (12) is tangent to the Euler curve at $\sigma=\frac{n}{n+2}\sigma_u$.

[6] The first of these has been used by K. Hohenemser (Zeitschrift für angewandte Mathematik und Mechanik, vol. 11, p. 15, February, 1931), the second has been used several times before and is obvious, and the third has been used by L. B. Tuckerman, the late S. N. Petrenko, and C. D. Johnson (National Advisory Committee for Aeronautics, Technical Note No. 307, Washington, D. C.).

With this value of C_n, in terms of the variables defined by (6), equation (12) becomes

$$s = 1 - \frac{2}{n}\left(\frac{n}{n+2}\right)^{1+\frac{n}{2}} \lambda^n \tag{13}$$

which applies for $\frac{n}{n+2} \leqq s \leqq 1$. Figure 1 shows the curves

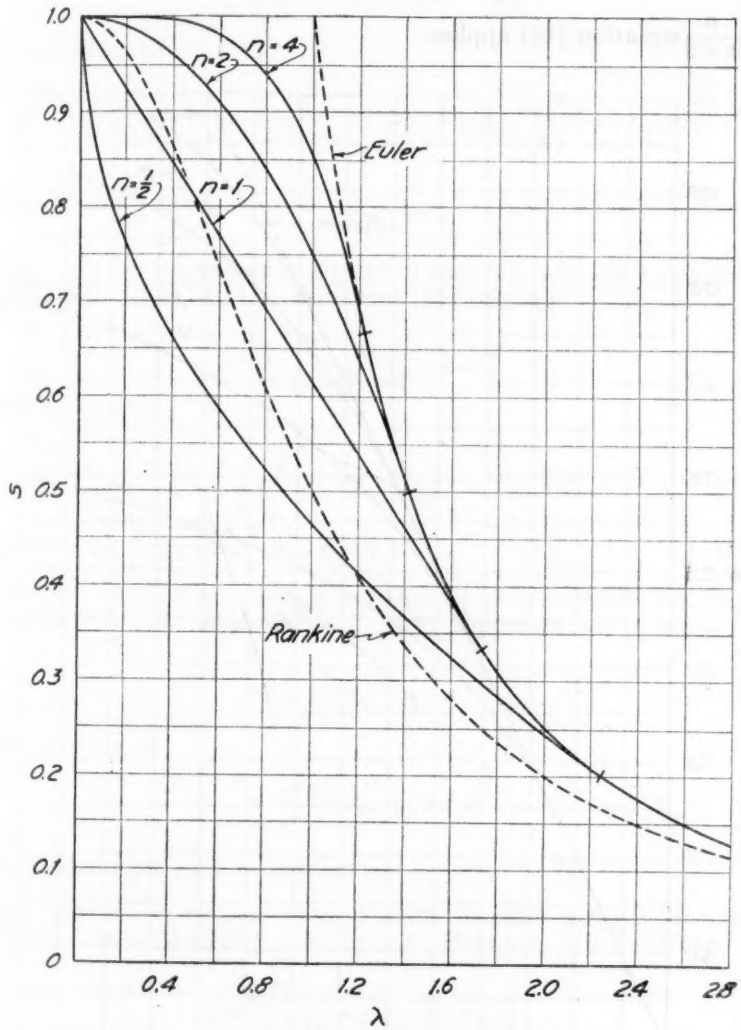

FIGURE 1.—*Reduced column curves of several types*

represented by equation (9) (marked Euler) and equation (13) for different values of n. Equation (13) solved for λ gives

$$\lambda = \left(\frac{n}{2}\right)^{\frac{1}{n}} \left(\frac{n+2}{n}\right)^{\frac{1}{n}+\frac{1}{2}} (1-s)^{\frac{1}{n}} \tag{14}$$

and substitution of this expression in equation (11) gives finally

$$e=2\left(\frac{2}{n}\right)^{\frac{2}{n}}\left(\frac{n}{n+2}\right)^{1+\frac{2}{n}}\int_{s_p}^{s}\frac{ds}{s(1-s)^{\frac{2}{n}}}-s+2s_p \tag{15}$$

for values of s from $\frac{n}{n+2}$ to 1, inclusive. For s less than or equal to $s_p=\frac{n}{n+2}$ equation (10) applies.

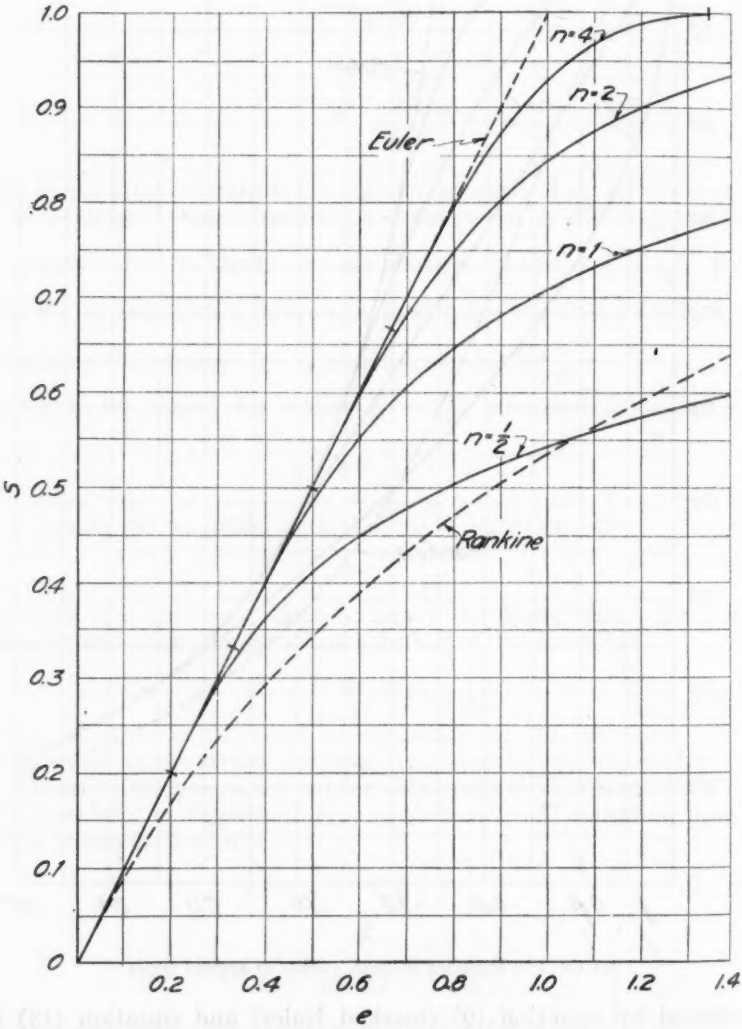

FIGURE 2.—*Reduced compressive stress-strain diagrams corresponding to the column curves of Figure 1*

Figure 2 shows the curves represented by equation (10) (marked Euler) and equation (15) for different values of n.

The case $n=\frac{1}{2}$ represents a column formula which experience has shown to be suitable for brittle materials like cast iron. (See fig. 1.) Equation (15) becomes

$$e=\frac{512}{3125}\int_{\frac{1}{5}}^{s}\frac{ds}{s(1-s)^4}-s+\frac{2}{5} \tag{16}$$

which reduces to

$$e=0.1638\left[\frac{1}{3(1-s)^3}+\frac{1}{2(1-s)^2}+\frac{1}{1-s}+\log\frac{s}{1-s}\right]-s+0.1877 \tag{17}$$

applicable for $\frac{1}{5}\leqq s\leqq 1$. (See fig. 2.)

The case $n=1$ represents a column formula suitable for common grade wood. (See fig. 1.) Equation (15) becomes

$$e=\frac{8}{27}\int_{\frac{1}{3}}^{s}\frac{ds}{s(1-s)^2}-s+\frac{2}{3} \tag{18}$$

which reduces to

$$e=\frac{8}{27}\left(\frac{1}{1-s}+\log\frac{s}{1-s}\right)-s+0.4276 \tag{19}$$

applicable for $\frac{1}{3}\leqq s\leqq 1$. (See fig. 2.)

The case $n=2$ represents a column formula suitable for ductile materials like mild steel. (See fig. 1.) Equation (15) becomes

$$e=\frac{1}{2}\int_{\frac{1}{2}}^{s}\frac{ds}{s(1-s)}-s+1 \tag{20}$$

which reduces to

$$e=\frac{1}{2}\log\frac{s}{1-s}-s+1 \tag{21}$$

applicable for $\frac{1}{2}\leqq s\leqq 1$. (See fig. 2.)

The case $n=4$ represents a column formula suitable for hard materials like hard steel. (See fig. 1.) Equation (15) becomes

$$e=\frac{4\sqrt{3}}{9}\int_{\frac{3}{4}}^{s}\frac{ds}{s(1-s)^{\frac{1}{2}}}-s+\frac{4}{3} \tag{22}$$

which reduces to

$$e=\frac{4\sqrt{3}}{9}\log\frac{1-\sqrt{1-s}}{1+\sqrt{1-s}}-s+2.347 \tag{23}$$

applicable for $\frac{2}{3}\leqq s\leqq 1$. (See fig. 2.)

The Rankine formula.—The Rankine formula

$$\sigma = \frac{\sigma_u}{1 + C_R\left(\frac{l}{i}\right)^2} \tag{24}$$

has been used for all values of $\frac{l}{i}$ with $C_R = \frac{\sigma_u}{\pi^2 E}$, in which case the curve represented by (24) approaches tangency to the Euler curve at infinity. With this value of C_R, in terms of the variables defined by (6), equation (24) becomes

$$s = \frac{1}{1+\lambda^2} \tag{25}$$

which solved for λ gives

$$\lambda = \sqrt{\frac{1-s}{s}} \tag{26}$$

and substitution of this expression in equation (11) gives

$$e = 2\int_0^s \frac{ds}{1-s} - s$$

or

$$e = -2 \log (1-s) - s \tag{27}$$

for values of s from 0 to 1, inclusive.

The curves represented by equations (25) and (27) are shown in Figures 1 and 2, respectively.

Appendix III shows an American Bridge Co. reduced straight-line column curve and the corresponding reduced stress-strain diagram.

All of the curves in Figure 2 except the curve marked $n = 4$ (equation (23)) approach the horizontal line $s = 1$ asymptotically. The curve marked $n = 4$ has a horizontal tangent at $e = 1.347$, $s = 1$. A comparison of the curves of Figure 1 with the corresponding curves of Figure 2 shows the type of compressive stress-strain diagram which is necessary in any particular case in order that a given column curve may represent accurately the strength of columns. The shapes of the reduced stress-strain diagrams are all reasonable except for high values of s and possibly in the case of the Rankine formula. The shape of the diagram for high values of s is relatively unimportant, however, since the corresponding portion of the column curve lies in the region of "short columns," and such columns do not usually fail by buckling. It is doubtful whether any structural material would show a reduced compressive stress-strain diagram like that required for the Rankine formula.

Viewed in another way, any (reduced) compressive stress-strain diagram in Figure 2 will yield the (reduced) column curve corresponding to it in Figure 1. If, therefore, the short-column strength, σ_u, of the material is such that, or can be defined (Appendix III) so that, the (reduced) compressive stress-strain diagram fits a curve of Figure 2, the column strength of the material will be given by the corresponding curve of Figure 1. It will frequently be possible by a suitable choice of σ_u to obtain good agreement between the actual (reduced) com-

pressive stress-strain diagram and one of the curves of Figure 2 up to some limiting value of s, beyond which the agreement will not be good. In that case the corresponding curve of Figure 1 will represent the column strength up to the same value of s. Thus, if representative compressive stress-strain diagrams of a material are available, it may be possible to draw the corresponding column curve without tests. This method is not to be recommended to the exclusion of tests, however, particularly not if the agreement between the actual (reduced) compressive stress-strain diagram and a curve of Figure 2 is not extremely good.

The author wishes to express his indebtedness to Dr. Walter Ramberg, of the engineering mechanics section, Bureau of Standards, for checking the equations.

APPENDIX I

Figure 3 shows the variation of $\frac{\overline{E}}{E}$ with $\frac{E'}{E}$ for a number of different cross sections, as listed on the figure. The curves for the thin circular-ring section (thickness negligible in comparison with the diameter) and the solid circular section are plotted from formulas by R. V. Southwell.[7]

The formula for the rectangular section is given by T. v. Kármán,[8] and the six points for the I section are taken from a graph by W. Gehler.[9] The two curves for the thin T section (thickness of the web and the flange negligible in comparison with their lengths) have been worked out by the author.

It may be noted that the curve for an unsymmetrical section may lie considerably below the curve for the idealized H section, and the lower limit for such sections is the curve $\frac{\overline{E}}{E}=\frac{E'}{E}$. (Fig. 3.) Consequently, Frandsen's treatment[10] may be considered as applying unmodified to unsymmetrical sections.

APPENDIX II

In interpreting column tests of ductile materials it is of some importance how σ_u is defined. If σ_u is defined as the stress determined by the intersection of the stress-strain curve with a line through the origin having a slope αE $(0<\alpha<1)$, the experimental points when plotted as a λ, s-diagram are likely to lie more nearly on a smooth curve than otherwise. Under ideal conditions of test (perfectly straight specimens, perfect centering, etc.) if different materials having affine stress-strain diagrams are tested, and if σ_u is determined as outlined, all points λ,s will lie on one and the same curve. In tests made at the Bureau of Standards the values $\alpha=\frac{5}{9}$ and $\alpha=\frac{2}{3}$ have

[7] Southwell (see footnote 1, p. 571.)
[8] Kármán (see footnote 1, p. 571.)
[9] Proceedings of the Second International Congress for Applied Mechanics, p. 366, Zurich, Sept. 12-17, 1926.
[10] See foot note 2, p. 571.

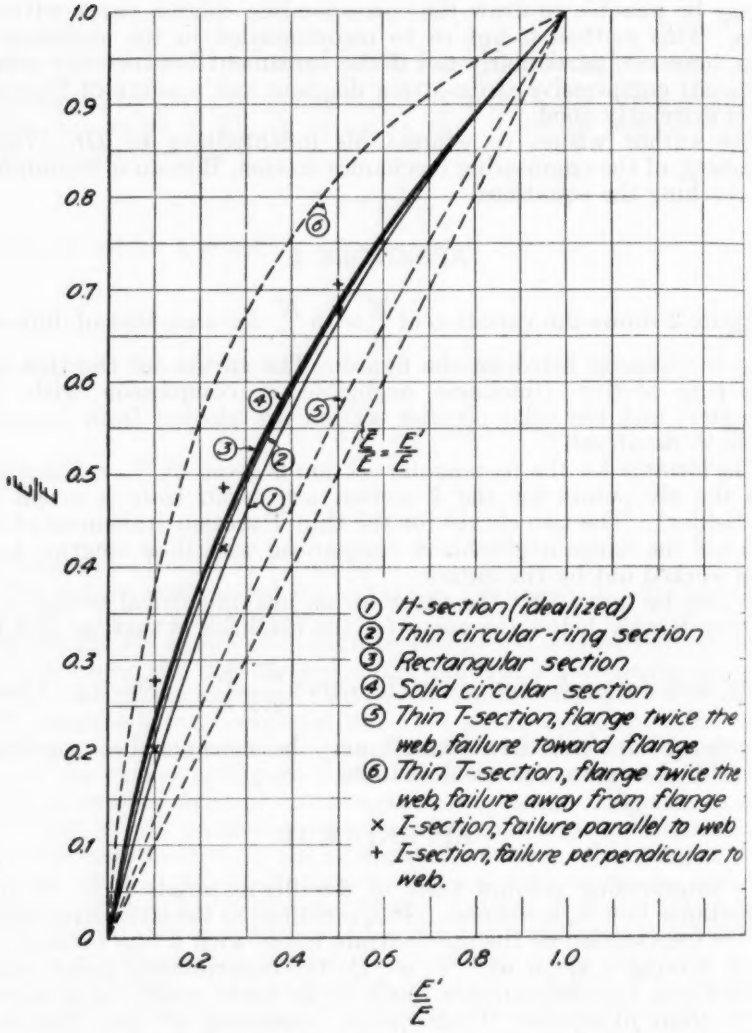

FIGURE 3.—*Variation of* $\frac{\overline{E}}{E}$ *with* $\frac{E'}{E}$ *for various shapes of cross section*

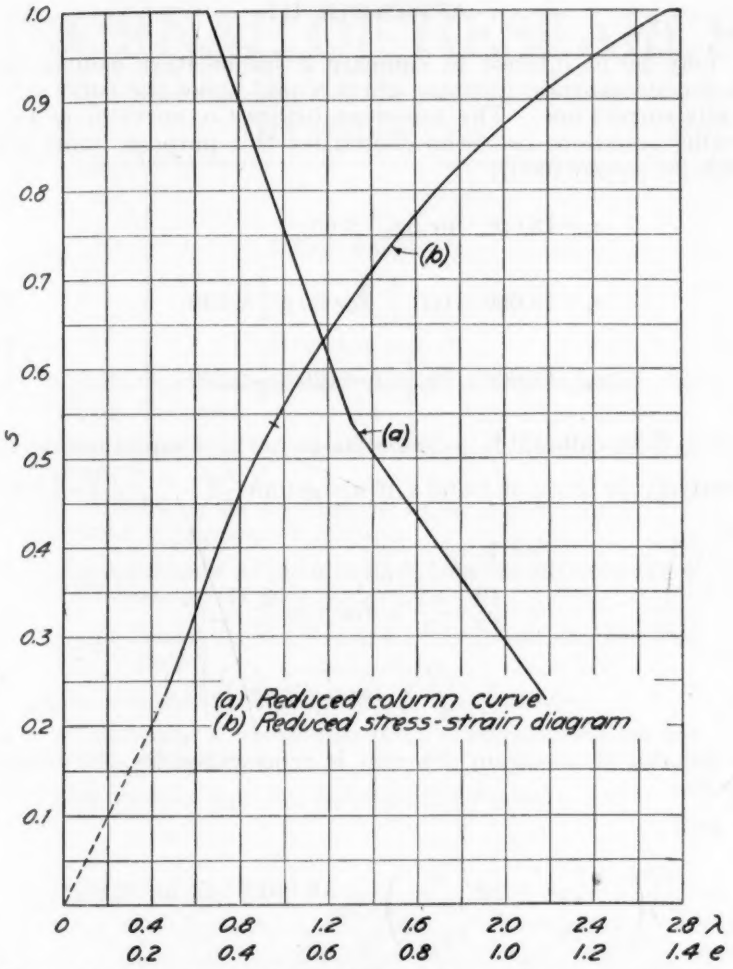

FIGURE 4.—*Reduced American Bridge Co. column curve and corresponding reduced compressive stress-strain diagram*

been found to give satisfactory results for chromium-molybdenum steel and duralumin columns, respectively.

By adjusting the value of α, it may be possible to fit the actual (reduced) compressive stress-strain diagram rather closely to one of the curves of Figure 2 up to a sufficiently high value of s to include all except short columns.

APPENDIX III

It may be of interest to compare a specification column curve with the stress-strain diagram which would make the curve a theoretically correct one. The American Bridge Co. curve given by the following equations has been chosen for this purpose (units are in pounds per square inch):

$$\left.\begin{aligned} \sigma_s &= 13{,}000 \quad \text{for } 0 \leqq \frac{l}{i} \leqq 60, \\ \sigma_s &= 19{,}000 - 100\,\frac{l}{i} \quad \text{for } 60 \leqq \frac{l}{i} \leqq 120, \\ \sigma_s &= 13{,}000 - 50\,\frac{l}{i} \quad \text{for } 120 \leqq \frac{l}{i} \leqq 200, \end{aligned}\right\} \tag{28}$$

where σ_s is the allowable average stress. These equations become, respectively, in terms of λ and s, if we assume $\frac{\sigma_u}{E}\left(=\frac{\pi^2}{8450}\right)=0.001168$,

$$\left.\begin{aligned} s &= 1, \\ s &= \frac{19}{13} - \frac{\sqrt{2}}{2}\,\lambda \quad \text{for } 1 \geqq s \geqq \frac{7}{13} \\ s &= 1 - \frac{\sqrt{2}}{4}\,\lambda \quad \text{for } \frac{7}{13} \geqq s \geqq \frac{3}{13} \end{aligned}\right\} \tag{29}$$

The reduced stress-strain diagram is represented by the following equations:

$$\left.\begin{aligned} s &= 1 \\ e &= \frac{169}{361}\left(\frac{1}{1-\frac{13}{19}\,s} + \log\frac{s}{\frac{19}{13}-s}\right) - s + 0.0913 + C \quad \text{for } 1 \geqq s \geqq \frac{7}{13} \\ e &= \frac{1}{4}\left(\frac{1}{1-s} + \log\frac{s}{1-s}\right) - s + C \quad \text{for } \frac{7}{13} \geqq s \geqq \frac{3}{13} \end{aligned}\right\} \tag{30}$$

where the constant of integration C is arbitrary.

Equations (29) and (30) are represented graphically in Figure 4.

WASHINGTON, July 14, 1932.